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PAPERS READ.

AUTOMATIC ZERO BURETTE.[1]

BY EDWARD R. SQUIBB, M. D.

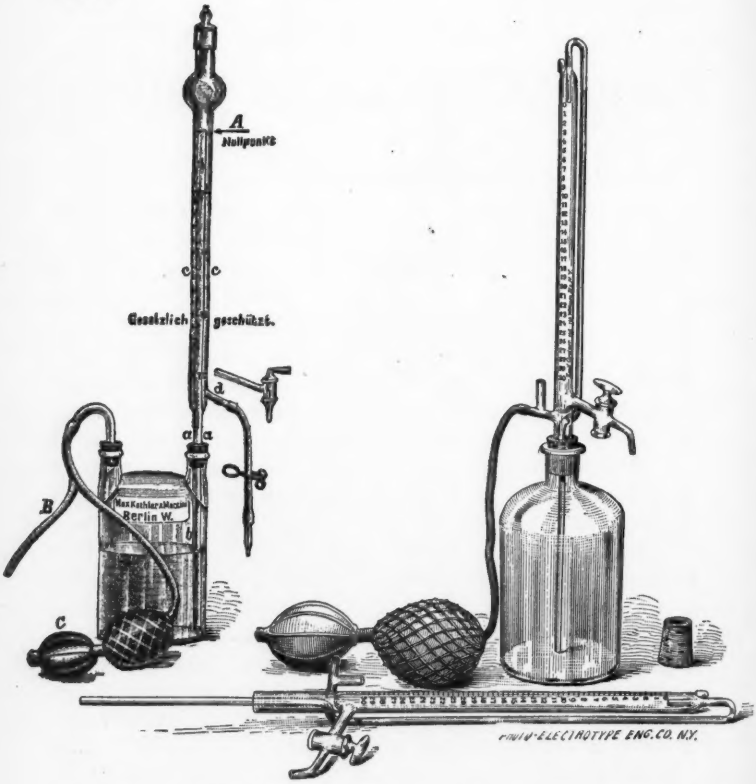
IN many manufactories and laboratories two or more volumetric solutions are in frequent use, and for such it is convenient to have a burette that can be rapidly used, and be carried about from place to place. This is practicable with the ordinary burette and stand. But then the bottle of volumetric solution has also to be carried about and much time is required in filling and adjusting to the Zero mark.

In the *Berichte der deutschen chemischen Gesellschaft* for October 24, 1892, No. 15, page 3010, Stanislaus Krawczynski has a description and cut of a new form of burette with an arrangement for automatic or mechanical filling to the Zero point. The cut of this apparatus is reproduced here in the left-hand group of the first illustration plate in order that the inventor may have due credit for the physical principles of which he has availed himself.

On having a couple of these made for trial the writer observed that solutions of different physical properties gave different levels in overflowing through the central tube and were not fairly constant to the zero mark. Messrs. Eimer and Amend, of New York, had one made in which the internal tube was turned over upon itself for about one cm. at the upper end and this gave a

[1] Read December 8, 1893.

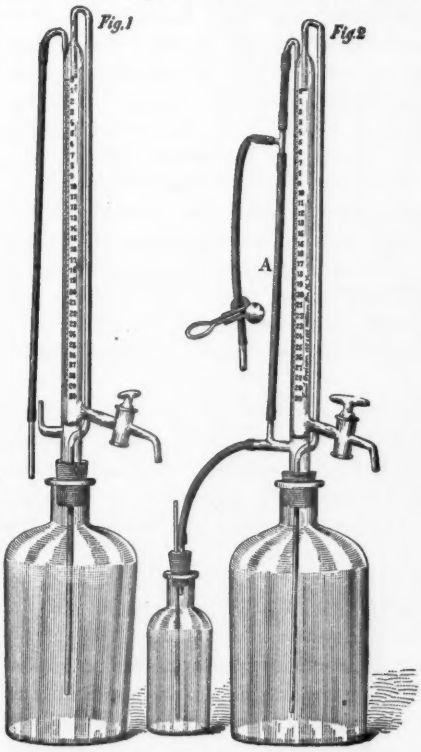
more uniform level with different solutions; and they substituted an ordinary Erlenmeyer flask of liter size for the two necked bottle.



But it was found impracticable to get the internal tube quite straight, and to have it exactly in the center of the outer graduated tube throughout its length, and the least variation in this condition gave a distorted meniscus. Then again the distortions were not uniform nor constant, but varied with the relations between the inner and outer tubes so as to disturb the values of the readings in different parts of the burette.

To overcome these disadvantages this writer simply put the filling tube from the bottle on the outside of the burette in the way shown in the right-hand group of the illustration. By this arrangement the excess of liquid blown over by the rubber pressure bulbs is siphoned off to the zero point with a fair degree of accuracy and uniformity after the finger is removed from the open end of the ⊥ tube on the left.

After a little experience with this modification it was easy to reach another that had still greater advantages over the last. In this the expensive and cumbersome rubber pressure bulbs are dispensed with, and the burette is filled by mouth-suction, just as an ordinary pipette is filled. The apparatus shown by Fig. 1, of the second cut shows this design in its simplest form, Here the suction is applied at the top of the burette, the filling liquid rising from the bottle through the outside tube until the zero mark is passed. Then on stopping the suction the excess of solution is siphoned off to the zero mark and flows back into the bottle. If the apparatus is to be set aside for any considerable length of time it may be closed against the external air by removing the glass mouth-piece from the suction tube,



and slipping the end of the rubber tubing over the turned up end of the glass tube by which air is admitted to the bottle to replace the solution drawn up the filling tube. But this is hardly necessary in any ordinary usage.

In many cases, however, it is necessary to exclude the carbon dioxide and other impurities of the laboratory air from volumetric solutions, and to prevent concentration of the solutions by evaporation of their water. These conditions are met in the modification shown in Fig. 2, of the second cut. Here a small wash-bottle is added, through which all the air admitted to the apparatus, either above or below, must pass, and be washed in passing. This bottle may be supplied with baryta water or lime water when it will serve to saturate the air through it with moisture, and free it from ordinary gases and vapors. In using this apparatus a pinch-cock is necessary on the rubber suction tube near the mouth-piece, by which the mouth-piece is conveniently handled, and during the suction this pinch-cock is opened and the rubber tube below is pinched at A by the thumb and finger of the left hand. This apparatus is constantly sealed from the external air, and is safe and accurate for any length of time, and is always in readiness for use, care being taken to well wash the end of the stop-cock, and to waste the solution that is outside of the cock whenever the apparatus has stood unused for even a few hours.

These burettes are very well made by Mr. Emil Greiner, of 146 William Street, near Fulton, New York City, who supplies them with or without the bottles as ordered. The only advantage in ordering the burette and bottle together is to have the internal tube of the right length to reach the bottom of the bottle.

A COMPRESSED AIR WASH-BOTTLE.[1]

By W. C. Ferguson.

THIS idea, not yet put in practical operation, was suggested by the difficulty attending the washing of such precipitates as hydrate of alumina, the complete removal of very small amounts of finely divided material from the sides of the contain-

[1] Read December 8, 1893.

ing vessels, such as gold in commercial copper, or of such precipitates as adhere with persistency, when the ordinary wash-bottle, with comparatively little pressure available, is used. It would also seem that such a device would facilitate the general washing of precipitates in a laboratory where sometimes a hundred or more filtrations are made in a single day.

The features of the idea are about as follows:

Compressed air would be the source of pressure, and in the laboratory of which the writer has charge it could be introduced very conveniently from the factory where it is used on a large scale. Mr. J. B. F. Herreshoff, the distinguished chemical engineer, suggested using a gasometer where no source outside of the laboratory was available.

The air pipe would be arranged with branches to the filter pumps, and also to any other part of the laboratory where filtrations would be carried on.

The wash-bottles would be large and stout, and the apparatus arranged so that they could be removed readily and refilled or replaced as required. The air pipes would be provided with stop-cocks, just above the bottle, for regulating the supply of air. Glass nozzles of about the same form and length as in the ordinary wash-bottle, but with orifices of different sizes would be used, so that a very fine jet or a large stream of water could be employed as desired.

Rubber tubing of suitable length and strength would connect the water-bottle and nozzle.

The jet would be further regulated by a pinch-cock just above the nozzle so as to be conveniently manipulated while washing.

The advantages of this device would seem to be a minimum amount of work in manipulation, and a more thorough washing due to increased pressure. Where a large amount of work is done each day and accurate, prompt reports are absolutely necessary, it is self-evident that all devices that reduce labor and in other ways increase efficiency, tend to raise the standard of results.

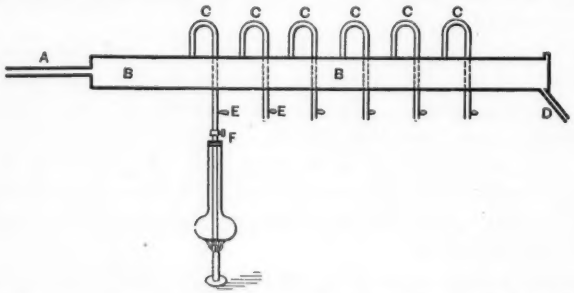
AN ARRANGEMENT FOR CONDUCTING A NUMBER OF LABORATORY DISTILLATIONS WITH STEAM, SIMULTANEOUSLY.[1]

By W. C. Ferguson.

A is an ordinary $\frac{3}{8}$ inch iron steam pipe connected with the steam system in the factory and provided with a valve where it enters the laboratory. B is a brass pipe $1\frac{1}{2}$ inches in diameter, connected with A and inclining towards D, to facilitate the removal of condensed water.

The tubes C, are about $\frac{1}{8}$ inch in diameter and are provided with cocks at E.

When distillations are in operation the brass tubes C are connected with glass tubes by means of rubber tubing; the glass



tubes reach nearly to the bottom of the distilling flasks and are provided with ground glass stop-cocks at F. D carries off the condensed water from B.

The entire apparatus is suspended from the ceiling by stiff iron rods. The condensers are arranged at right angles to, and immediately underneath B. The table is provided with both cold water and waste pipes for the condensers.

B must be high enough to permit the use of Bunsen burners under the distilling flasks.

Before starting distillations, all of the cocks E, must be opened and steam turned on, to blow out condensed steam; they are then closed, the distilling flasks connected as described above

[1] Read December 8, 1893.

and the cocks E again opened, taking care to have the ground glass cocks F closed.

During distillation the steam is controlled by the stop-cocks F, and the operation is further regulated by the use of Bunsen burners under the distilling flasks. One person can easily attend to six or more distillations at one time.

Experience of more than a year has proved the utility of this arrangement, where many samples involving analysis by distillation, have been presented in a day.

A NEW MUFFLE FOR INCINERATION OF SUGAR.[1]

By H. Schweitzer and E. Lungwitz.

THE incineration of sugar for the determination of ash is generally carried out in platinum dishes which are placed in a muffle of platinum (Scheibler) or of Russian sheet iron (F. G. Wiechmann) kept at a dull red heat. The platinum muffles to hold two dishes, weigh from sixty to seventy-five grams, and are very expensive apparatus. Moreover it happens very often that in a platinum muffle the last portions of carbon are oxidized with difficulty. Frequently a little higher temperature under the muffle of platinum which is such an extremely good conductor of heat, causes the ash to fuse and the melted salts, including unburnt carbon, form black blotches in the dish. On account of the insufficient draught in the platinum muffle it is then very difficult to accomplish perfect incineration. In such a case, as Tucker says in his manual of sugar analysis, the dish is allowed to cool, one or two drops of sulphuric acid added, and the dish heated cautiously at first to avoid spattering and finally brought to redness for fifteen minutes. Naturally such proceeding causes delay and does not contribute to the exactness of the determination.

The muffles of iron are impracticable for quick commercial work because the incineration in them takes much longer time than in those of platinum.

These considerations prompted us to devise an apparatus, better fitted for the incineration of sugar than the muffles mentioned above.

Read December 8, 1893.

The accompanying cuts show how we solved this problem.

A French clay muffle is cut open at the bottom; (see Fig. 1, *a*, *b*) through the walls of the muffle at both ends holes are bored (Fig. 2, *c*, *d*) through which platinum wires are fastened in the manner shown in Fig. 1, *c*, *f*. These wires serve as support for the bent platinum sheet, (Fig. 1, *w*, *x*, *y*, *z*) on which the dishes containing the sugar are placed. In the center of the top of the muffle a round hole is cut out, (Fig. 3, *t*). The bent sheet *w*, *x*, *y*, *z*, can also be made of Russian sheet iron. The muffle is placed on a tripod and heated as usual.

FIG. 1.

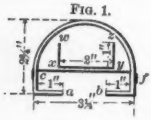
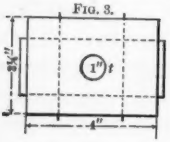


FIG. 2.

FIG. 3.



This construction produces a good draught in the muffle and allows the use of the largest flame of the so-called "Acme" burner which accelerates the incineration very considerably. Whereas the complete incineration under normal conditions in a platinum muffle lasts from about forty to forty-five minutes, it lasts only twenty-five to thirty minutes in our platinum clay muffle and about forty-five minutes in our platinum iron muffle. The short time in which our platinum clay muffle works, naturally reduces the expense for gas. For about one year we have had both kinds of clay muffles in constant use and always obtain light and flaky ash and never a fused ash.

We feel assured that these new muffles, saving time and money, will be welcome additions to the outfit of every sugar laboratory.

LABORATORY OF DR. H. SCHWEITZER,
159 FRONT STREET, NEW YORK CITY.

A FEW REMARKS ABOUT BASIC SULPHATE OF ALUMINA.[1]

By W. C. Ferguson.

MANY samples of commercial sulphate of alumina contain more or less of an excess of alumina over that required to form the normal sulphate ($Al_2(SO_4)_3$), the amount varying from a trace to $2\frac{1}{2}$ per cent. and occasionally even more.

The following composition is of frequent occurrence:

Total soluble alumina = 17.00 per cent.; soluble alumina calculated from sulphuric anhydrate (SO_3) to form $Al_2(SO_4)_3$ = 15.2 per cent., leaving 1.8 per cent. of alumina in excess of that required to form the normal sulphate.

It is concerning the probable chemical constitution of this alumina in excess of that required to form the normal sulphate, together with its behavior towards resin soap in the manufacture of paper, that this brief article is written.

As is well known, in sizing paper sulphate of alumina is made to react on resin soap (made by saturating soda ash with resin), thus precipitating an insoluble alumina soap, a resinate of alumina in the fiber of the paper.

In many paper works the per cent. of normal sulphate $Al_2(SO_4)_3$ determines the strength of the material bought and, other things being favorable, that is preferred which contains the highest per cent. of $Al_2(SO_4)_3$.

A number of reports from paper mills are about as follows:

$$\left\{\begin{array}{l} \text{Combined } Al_2O_3 = 15.20 = Al_2(SO_4)_3 = 50.96 \\ \text{Free } Al_2O_3 \quad = \ 1.80, \text{ or} \end{array}\right.$$

$$\left\{\begin{array}{ll} Al_2(SO_4)_3 & = 50.96 \\ Al_2O_3 & = \ 1.80 \end{array}\right.$$

In such reports the "combined" Al_2O_3 and also the $Al_2(SO_4)_3$ are calculated from the SO_3 present and the soluble so-called "free" Al_2O_3 is ignored as being of no value for sizing purposes. This idea that has so little, if anything, to support it, is discussed below.

A solution of normal sulphate of alumina behaves very much

[1] Read January 12, 1894.

like an acid; it combines with bases, evolves hydrogen with metals, and is acid to litmus paper. We should, therefore, expect SO_3 to combine with more alumina than is represented by the normal sulphate, and it might be added that as weak bases have the characteristic of forming basic salts, we should for this reason also anticipate the formation of basic sulphates of alumina. These basic sulphates can readily be formed in the laboratory from the normal sulphate.

1. By dissolving alumina in the normal sulphate.

2. By action of caustic alkalies on a solution of the normal sulphate. $Al_2(SO_4)_3+Na_2O=Al_2O_3(SO_3)_2+Na_2SO_4$.

For example: A solution of normal sulphate of alumina containing seven per cent. of alumina can be made two per cent. basic by adding caustic soda slowly to a hot solution until a precipitate forms that does not dissolve even on long boiling. This is equivalent in a seventeen per cent. material to having 4.86 per cent. in excess of that required to form $Al_2(SO_4)_3$.

3. By action of a metal, $Al_2(SO_4)_3+Zn+H_2O=ZnSO_4+Al_2O_3(SO_3)_2+H_2$.

These equations are only intended to illustrate the probable types of reaction; it is not assumed that just such compounds are formed.

The following standard works treat of a number of basic sulphates of alumina that are soluble in water:

"Watts' Dictionary of Chemistry,"
"Roscoe & Schorlemmer's Chemistry,"
"Mendelejeff's Principles of Chemistry."

A careful search through the literature fails to reveal any reference to "free" alumina existing in a solution of normal sulphate.

The term "free" implies the reverse of combined and from the considerations given above it is not deemed best to call the alumina contents in excess of that required to form normal sulphate "free" with every condition favoring combination. Such alumina is undoubtedly combined as basic sulphate and being in solution there is every reason to believe that it would form a resinate of alumina with resin soap as readily as the normal sulphate, and some ground for the assumption that it might be even more available because it is probably held in weaker combination

and so would be more readily decomposed and precipitated as size; and if this were true such basic alumina would be more valuable than the normal because more would be precipitated by a given weight of resin soap. With these considerations in mind the following investigations were carried out in the laboratory. In order to observe the action of resin soap on a solution in which the alumina approaches nearest to the free state some aluminate of soda was prepared by dissolving alumina in caustic soda. In this solution alumina is so feebly held in combination that the weakest acids, such as carbonic, will replace it. The solution is basic, and alkaline to test paper.

Resin soap immediately precipitates a voluminous precipitate of resinate of alumina. Even upon the addition of a drop or two of resin soap the precipitate begins to form.

A comparison of a neutral sulphate containing seventeen per cent. soluble alumina and of a basic sulphate containing seventeen per cent. total soluble alumina, fifteen per cent. being normal and two per cent. being basic, the so-called "free," were each treated with an equal amount of resin soap in such a quantity that but a portion of the alumina was precipitated. The solutions were filtered and precipitates washed with equal amounts of water and ignited. It was found that under such conditions

4.40 grams were precipitated from the neutral solution,
6.98 grams were precipitated from the basic solution.

These results are what theory would anticipate.

A brief summary of the case is this: It would seem that there is no "free" soluble alumina in the basic sulphate of alumina of commerce; such alumina is in direct combination as basic sulphate and being more feebly held in combination than alumina combined as normal sulphate, more readily forms size with resin soap and is therefore more economical, less resin soap being required for a given weight of sulphate. It directly follows from this that in any sulphate of alumina the $Al_2(SO_4)_3$ should be calculated from the total soluble alumina and *not* from that combined as normal sulphate alone, as in the latter case the most valuable alumina content is ignored as being useless. The following example will serve to illustrate the difference in value based on the two types of analyses: In a sulphate of alumina analyzing

Total soluble alumina	17.00 per cent.
Alumina combined as normal	15.20 " "
Basic alumina = so-called "free"	1.80 " "

The $Al_2(SO_4)_3$ calculated from 15.20 per cent. of alumina equals 50.96 per cent., whereas if calculated from 17.00 per cent. the $Al_2(SO_4)_3$ equals 57.00 per cent. In conjunction with these figures it must be borne in mind that experiment proves the basic sulphate of alumina to be relatively even more efficient than the difference in the above interpretations of analysis indicate.

DROPPING FLASK FOR STANDARD SOLUTIONS.[1]

By Frank Vanderpoel.

IT is well known that in working with standard solutions, the strength of the latter, when determined by the volume used, is influenced by the temperature to quite an appreciable extent. In fact, if a solution be standardized at 25° C. and afterward used at 20° C., its strength at the latter temperature is 10.01 times what it was at the former. For this reason it is necessary when employing volumetric apparatus to note the temperature of the solution if very accurate work be done.

Again it has been observed that burettes and delivery pipettes sometimes vary in the volume of liquid delivered, this variation depending upon the nature of the solution or the ease with which it wets the sides of the glass tube, as all solutions are not the same in this respect.

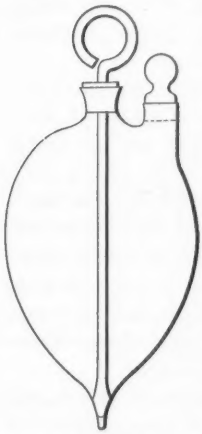
With an apparatus so made, however, that the standard solution is weighed instead of measured, these objections disappear, while accuracy is not impaired; in fact, with a common balance, sensitive to one centigram, much finer work can be done by weighing the solution than by measuring with a burette which reads to tenths of a cubic centimeter.

A number of dropping flasks and bottles have been invented from time to time with the above object in view; the one here represented having been devised some four or five years ago and kept in constant use in my laboratory ever since. It is quite simple and consists of a cylindrical or globular flask provided with two openings at the top and a dropping tube at the bottom

[1] Read December 8, 1893.

into which a glass rod is ground so as to make a tight joint. The rod runs through a perforated stopper in the central opening at the top in order that it may be kept in proper position. The second opening at the top is used when it is necessary to fill the bottle.

The apparatus may be supported by a small light tripod upon the pan of the balance, or it may be provided with two small hooks of brass wire fastened to a collar of the same metal which encircles the upper central tubulus. By means of these hooks the bottle is easily and quickly suspended from the bows supporting the balance pans.



I make use of a common pulp scale with four inch pans, and after counterpoising the filled bottle by means of brass cup weight supplemented by fine shot, perform the titration, and upon its completion determine the amount of liquid used by adding weights to that side of the balance from which the bottle is suspended. This necessitates but one calculation. The bottle may be used for solution of potassium permanganate or silver nitrate or in fact any solution which is generally employed in a burette furnished with a glass stop-cock.

It is very readily taken apart, cleaned and dried.

NEWARK, N. J.

ON THE ESTIMATION OF POTASSIUM IODIDE AND SODIUM ACETATE IN THE PRESENCE OF COMPLEX ORGANIC MIXTURES.[1]

BY JAMES H. STEBBINS, JR., PH.D.

I RECEIVED a short time since a sample of medicine for examination, which on qualitative analysis was found to contain potassium iodide and sodium acetate together with certain complex vegetable extracts, and as the determination of the first two named compounds gave me a great deal of trouble before a

[1] Read January 19, 1894.

satisfactory method of analysis was found, I thought that an account of the process finally adopted, though containing no great novelty, might be of assistance to some of my colleagues should they ever by chance have to examine a mixture of this kind.

Potassium Iodide.—This compound was determined as follows without any trouble:

Ten cc. of medicine were diluted with 100 cc. of distilled water, and the salmon colored flocculent precipitate formed collected upon a filter.

After thoroughly washing the filter out with cold water, the iodine in the filtrate was determined as usual as iodide of silver and then calculated to iodide of potassium. The amount of the latter compound found was 3.58 per cent.

Sodium Acetate.—It was first sought to determine the acetic acid in the mixture as such in the usual way, by distillation with sulphuric acid, and from the quantity so found to calculate the percentage of sodium acetate present, but it soon became evident that this process could not be used, as the sulphuric acid was found to liberate iodine as well as acetic acid whose estimation was thus rendered impossible.

It was next sought to arrive at the percentage of sodium acetate by an examination of the ash left after igniting the dry extract. But unfortunately the usual method of incineration was found to be of no avail, as by this process the sodium acetate is either wholly or partially converted into sodium carbonate, no uniform products being obtainable, and the potassium iodide is likewise subject to decomposition and volatilization. Moreover it was found impossible to obtain an ash absolutely free from carbon, it always being necessary to treat the ash after ignition with water to free it from a small carbonaceous residue and then to ignite this residue a second time, to add its ash to the aqueous solution, to evaporate the whole to dryness, and to determine the per cent. potassium and sodium present as sulphates by the well-known process of indirect analysis.

As, however, no satisfactory conclusions could be reached in this way the following method was finally adopted:

Ten cc. of fluid extract were pipetted off into a capacious platinum dish and mixed with thirty cc. of twenty per cent. sulphuric

acid. The contents of the dish were now evaporated upon a steam-bath to the consistency of a thick syrup. The dish was then transferred to a sand-bath and gently heated until the contents had charred and no more fumes of sulphuric acid or iodine were given off. A compact carbonaceous mass will thus be obtained, which contains all the sodium and potassium in the fluid extract as sulphates. The contents of the dish were now moistened with ammonium nitrate solution evaporated to dryness over the steam-bath, and then ignited over the direct flame of Bunsen burner.

The carbon will in this manner be completely consumed, leaving a perfectly white residue of sodium and potassium sulphates, which are then further examined by the process of indirect analysis.

In the present case the sum of the sulphates of potassium and sodium, from ten cc. of fluid extract, was 0.2499 gram.

The amount of SO_3 contained in the 0.2499 gram of sulphates was 0.1208 gram, or eqivalent to:

Sodium sulphate	0.57 per cent.
Potassium sulphate	1.92 " "

On now calculating the sodium sulphate to sodium acetate, and the potassium sulphate to potassium iodide, we get:

Sodium acetate	0.65 per cent.
Potassium iodide	3.65 " "

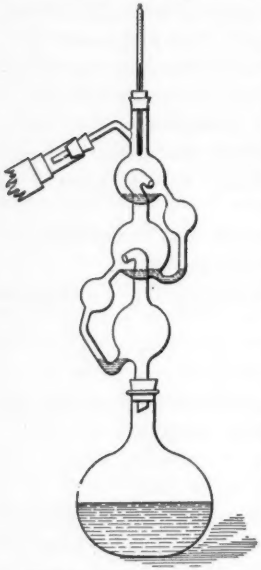
In the direct determination of the potassium iodide, as iodide of silver, we obtained 3.58 per cent. potassium iodide; hence it will be seen that the agreement between the direct and indirect methods of analysis is considering the complexity of the mixture under examination very satisfactory.

NEW YORK,
NOVEMBER 19, 1893.

APPARATUS FOR FRACTIONAL DISTILLATION.[1]

By C. W. Volney.

THIS apparatus for fractional distillation of mixtures of liquids of different boiling points is constructed on the dephlegmator principle. Although the opening of the recurved main tube is never closed by the condensed liquid, comparatively only small quantities of vapors of the liquids, condensable in the respective bulbs, ascend or ultimately escape in the condenser, so that by a second distillation liquids of practically uniform boiling points are obtained.



I have used this apparatus for the preparation of paraffins and benzene derivatives, and can recommend it as a good and practical instrument. The principle employed is evident from the figure, and any glass blower can make it.

New York,
November 23, 1893.

[1] Read December 8, 1893.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(*Continued from* 15, 181, *1893*.)

By Thomas B. Stillman, Ph.D.

NO standard specifications for the testing of Portland cement are required in Great Britain, the determination of fineness, tensile strength and variation in volume, being considered sufficient to determine the value of a cement. The machines for

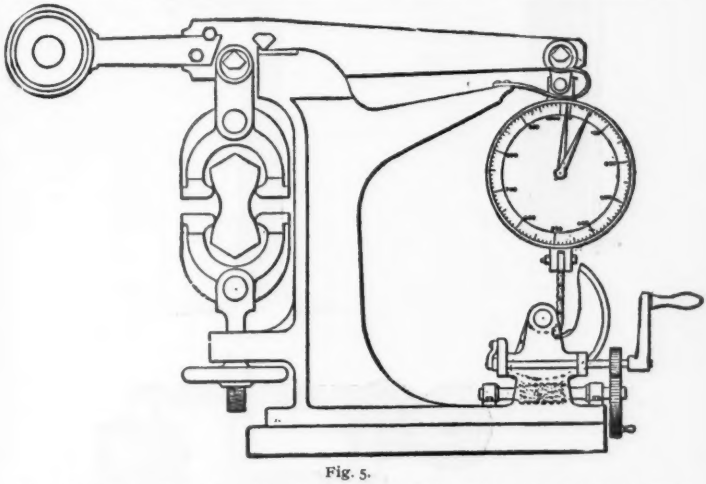


Fig. 5.

tensile strength are the "Faija" (Fig. 5) the "Reid and Bailey" (Figs. 6 and 6*a*), or the "Grant," the latter described in *Proceedings* of the Institution of Civil Engineers, **62**, 113. The "Reid and Bailey" is essentially the "Michaelis" (Fig. 4), excepting that water is used instead of fine shot for the breaking power.

It is readily seen that the "Faija" and "Grant" machines, not being automatic, require the application of the power at a certain uniform speed to obtain comparable results, since a difference of twenty-five per cent. in tensile strength may be obtained by applying the strain very quickly or very slowly (*Proceedings* of the Institution of Civil Engineers, **75**, 225, 226).

Fig. 6.

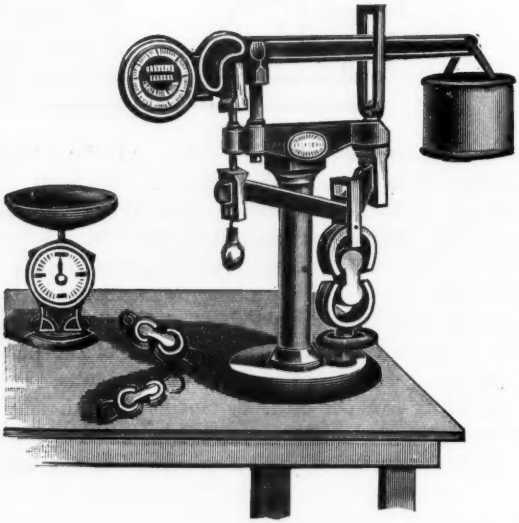


Fig 6*a*.

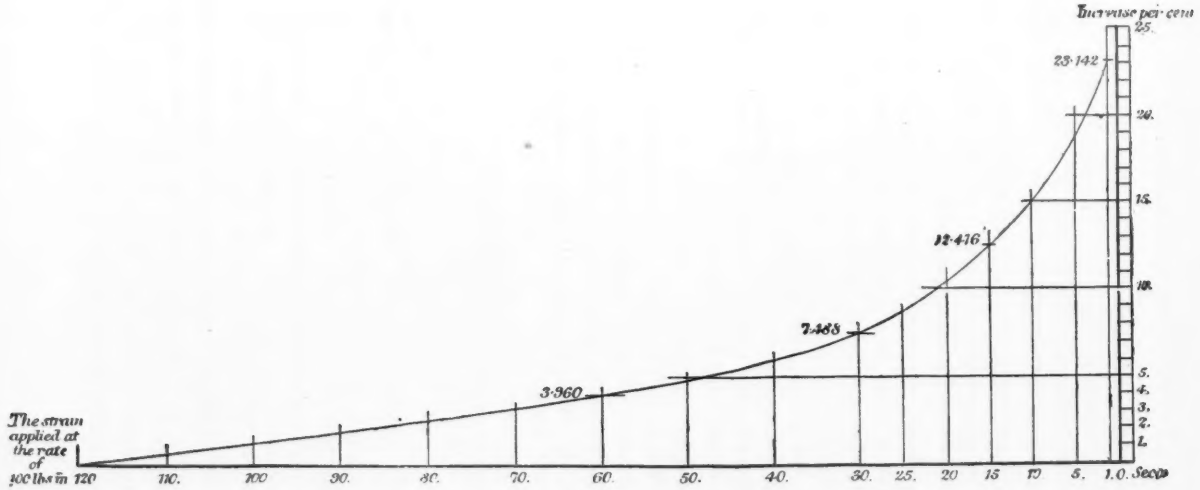

Increase per cent
25.
23·142
20.
15.
12·476
10.
7·488
5.
4.
3.
2.
1.
3·360
The strain applied at the rate of 100 lbs in 120
110.
100
90.
80.
70.
60.
50.
40.
30.
25.
20
15
10
5.
1.0. Secon

Fig. 7.

Faija has determined this variation with extreme care, the result being indicated in the curve shown in Fig. 7. To overcome these variations a uniform speed of 400 pounds per minute has been accepted as the standard.

Not only are comparable methods required in the use of the machines to obtain uniform results, but the briquettes must also be constructed under similar conditions.

It is manifestly unjust to compare the tensile strength of two cements (even when the briquettes are broken upon the same machine) unless the briquettes have the same weight of water for mixing; the same pressure with the trowel when being formed in the molds, and the same length of time of exposure under water before submitting the briquettes to the tensile strain. Usually the greatest difference is due to the pressure exerted in forming the briquettes.

For instance: Comparing tests made upon the Dyckerhoff Portland cement by Dr. Böhme, Director of the Royal Commission for testing building materials, at Berlin, and by E. J. De Smedt, General Inspector Engineer Department, District of Columbia, we find that the German method gives a much higher tensile strength than the method in use in this country.

DR. BÖHME.

Age of Briquettes.	Average tensile strength per square inch.	Number of tests.
7 days	767 pounds	10
28 "	895 "	10

E. J. DE SMEDT, C. E.

Age of briquettes.	Average tensile strength per square inch.
5 days	250 pounds
30 "	700 "

Showing:

109 pounds increase per day (7 days), Dr. Böhme,
50 " " " " (5 days), De Smedt,

or over 100 per cent. difference upon the same cement.

These variations are undoubtedly due principally to the different pressures upon the cement during the making of the briquettes, and to overcome difficulties of this nature the Vereins deutsche Portland Cement Fabrikanten have modified the rules in the construction of the briquettes so that two methods are acceptable:

First. The normal method, above given, with the trowel, etc., ("Handarbeit").

Second. The use of the Böhme-Hammer apparatus or "machine method," by which the cement in the briquette form

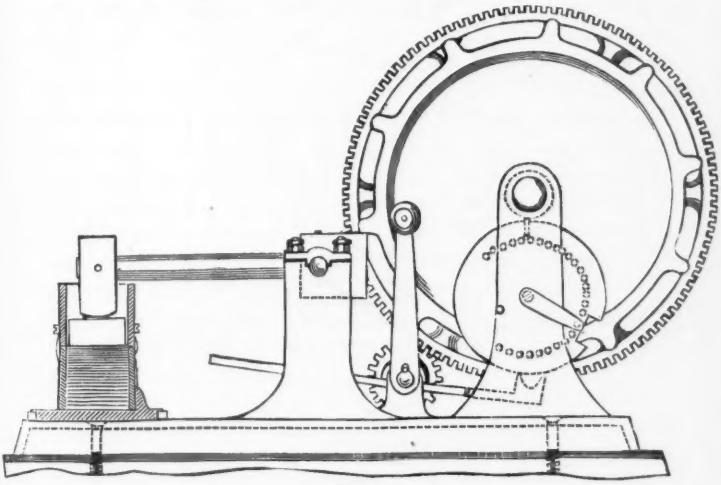


Fig. 8.

(after mixing with proper amount of water), is submitted to a pressure of 150 blows from a hammer weighing two kilos (Fig. 8). The briquette of cement is then removed from the mold and treated for tensile strength as usual.

This subject is receiving considerable attention at the present moment, the evident purpose being to render the test of tensile strength as uniform as possible by making the working of the apparatus automatic and the production of cement briquettes with the least possible variation in the pressure in the molds.

In this case no matter how careful the experimenter may be, the "personal equation" enters largely into the results of testing hand-made briquettes, for which reason the manufacture of the briquettes should be as automatic as possible. In no other way can results obtained by different experimenters be compared.

Prof. Charles D. Jameson describes an apparatus for this purpose (Fig. 9). *Transactions* of the American Society of Civil Engineers, **25,** 302.

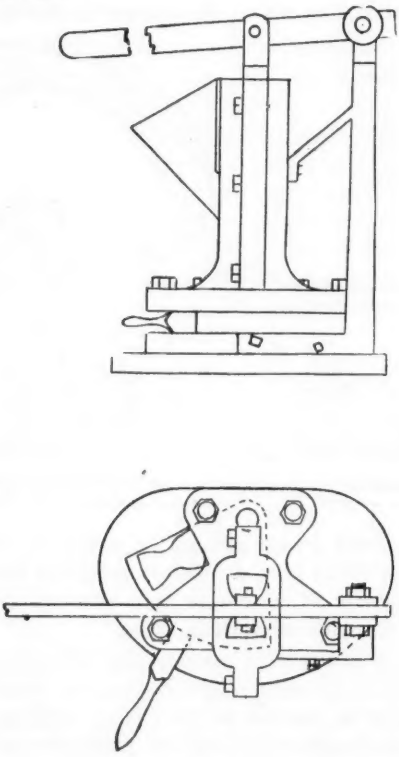


Fig. 9.

The method of operating is as follows: the lever being raised so that the lower end of the piston or main plunger is above the hole in the side of the cylinder communicating with the hopper, cement is put in the hopper and pushed down into the cylinder. The molding plate is pushed against one of the stops, so that one of the openings is beneath the bore of the cylinder. The long lever is forced down, causing the

plunger to force the cement into the opening in the molding plate. After this, the molding plate is swung against the other stop, cutting off the briquette, placing it over the plungers, throwing the other opening in the molding plate directly beneath the cylinder. The smaller lever is lifted, raising the plunger, and forces the briquette out of the mold, after which it is removed. The plunger is then pressed down, the main lever also, the molding plate swung back to the first position, the other plunger lever lifted, and another briquette is ready to be taken away, and so on. After making three briquettes, the main lever is lifted and more cement placed in the cylinder. The machine is best operated by two men, one to feed and operate the long lever, and the other to swing the molding plate, remove the briquettes, and lower the plungers. The pressure on the briquette is 175 pounds per square inch.

The conditions required in France for a good cement are:[1]

First. Analysis to determine the chemical composition.

Second. The determination of density.

Third. The determination of fineness.

Fourth. The determination of tensile strength.

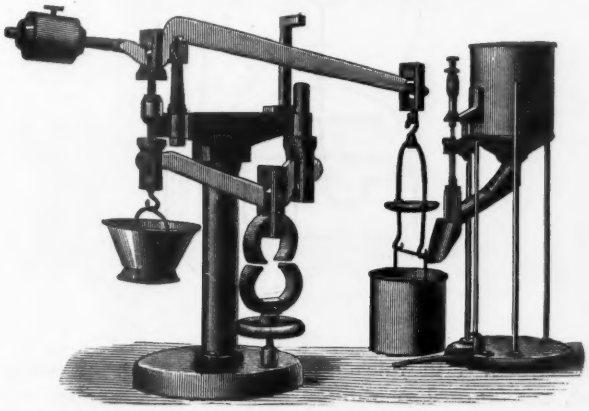


Fig. 10.

Fifth. The determination of crushing strength.

[1] E. Candlot, *Ciments et Chaux Hydrauliques*, Paris, Baudry and Co., *1891*.

Sixth. The determination of variations in volume.

The tensile strength is determined by the use of a Michaelis machine, Fig. 10, or the use of a Buignet apparatus, Fig. 11, this latter being upon an entirely different principle than any yet in use, and is thus described by the designer, M. Buignet, Conductor des ponts et chaussées au Havre:

It is composed of a basin A and frame B.

The basin A, filled with mercury and water, closes up by a diaphragm of rubber covered with a metallic disk, and is in direct communication with:

(*a*) Manometrique tube D.

(*b*) With a movable reservoir R, filled with mercury, by means of a rubber tube T.

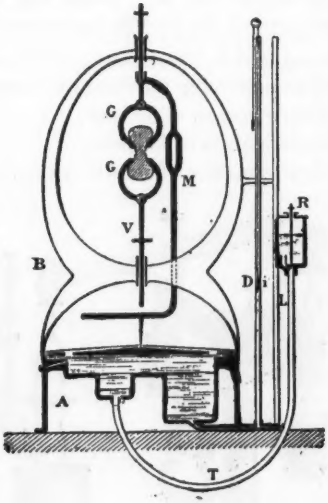


Fig. 11.

The grips G G, in which are to be placed the briquettes to be tested, are fastened, one to the frame B by the support V, the other to the support M, which rests upon the centre of the metallic disk over A. It is operated as follows: The briquettes are placed in the grips G G, and the support V moved up or

down until equipoise is established, and then firmly secured by a crank in frame B.

The support M is adjusted until the point at its lower end just touches the metallic disk in A.

By gradually lowering the resevoir R an upward pressure is given to the metallic disk in A, which is transferred to the support M, until when sufficient pressure is exerted the briquette is broken. The moment rupture of the briquette, takes place, the pressure required to do this is indicated by the float *i* in the manometer tube D.

Another instrument made use of to determine tensile strength, and used at l' ecole des ponts et chaussées, Paris, is shown in Fig. 12.

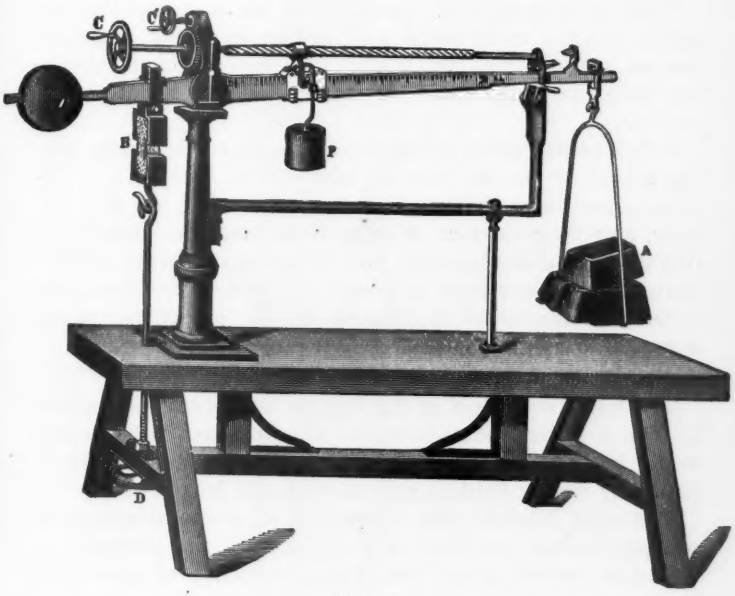


Fig. 12.

It is similar in principle to the Riehle machine (Fig. 2), and the Grant machine (*Proceedings* of the Institution of Civil Engineers, **62,** 98).

By a comparison of the various machines used in Germany, England, France, and the United States, we find practically but two in general use. The "Michaelis" (Figs. 4, 10, and 1), and the "Grant" (Figs. 2 and 12). While nearly all engineers require cements to be subjected to the tensile strength test, in fact relying more upon this one test than any of the others, it might be well to include here the opinion of H. Le Chatelier, professor at the École des Mines, Paris, France, as given in a paper presented at the last meeting of the American Institute of Mining Engineers, August, 1893, entitled "Tests of Hydraulic Materials." p. 44.

"The method of tension is at present most widely used, but the preference for it is not well founded.

"Here as in rupture by bending, only the *surface* of the briquettes acts in a really useful way, and its inevitable irregularities and alterations so greatly affect the precision of the results that they can in no case be trusted nearer than about twenty per cent.

"This preponderant influence of the superficial parts was first shown by the fact that the resistance of briquettes of different sizes increases, not with the section, but, on the contrary, with the perimeter. Finally, M. Durand-Claye has shown that the interior of a briquette may be removed without notably diminishing its resistance to rupture by tension, and has given a complete theoretical explanation of the phenomena which seemed at first sight paradoxical."

THE CRUSHING TEST.

This test is not official in this country and is seldom required by our engineers, who, however, have confined their experiments in this direction mainly to crushing tests of concrete, formed by mixing Portland cement, sand, and broken stone.

Test upon cubes of neat cement and of mortar composed of one part cement and three of standard sand, are generally included in reports given upon the examination of cements in Europe, the ratio being that the crushing strength is about ten times greater than the tensile strength.

Thus, a cement of good quality should show the following resistances per square centimeter:

TENSILE STRENGTH.

	7 days.	28 days.
Neat cement	25 kilos	35 kilos.
1 part cement, 3 parts sand . . .	10 "	18 "

CRUSHING STRENGTH.

	7 days.	28 days.
Neat cement	250 kilos	350 kilos
1 part cement, 3 parts sand . . .	100 "	180 "

To convert kilos per square centimeter to pounds per square inch, the equivalents used are: one kilo = 2.204 pounds English; 6.451 square centimeters = one square inch English.

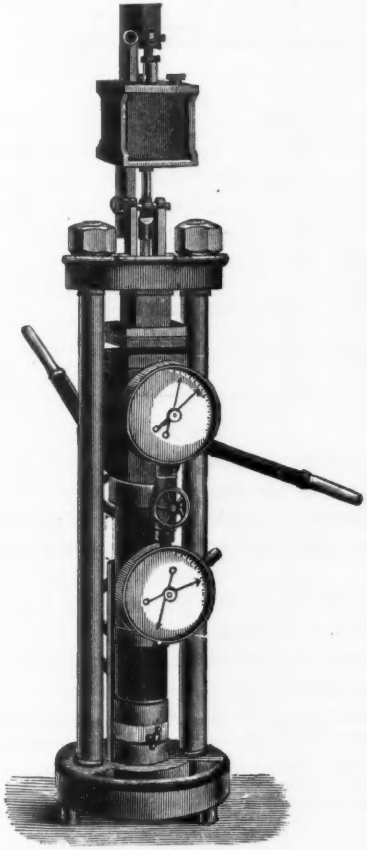


Fig. 14.

The hydraulic presses made use of for this purpose, a few years since, gave very discordant results, as it was impossible to distribute the pressure evenly over the surface of the cubes. This has been overcome, and there are now four machines upon the market whose results are comparable, *viz.:*

The "Suchier," Fig. 14; the "Böhme," Fig. 15; the "Tetmajer," as improved by Prof. Amsler-Laffon,[1] and the "Brink and Hubner."[2]

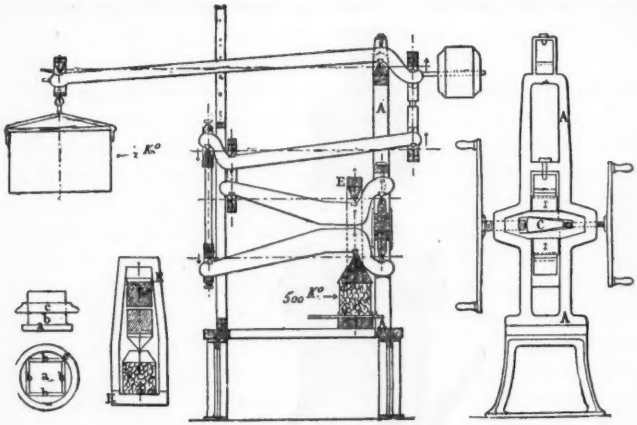


Fig. 15.

Variation in volume (expansion or contraction).—The method of Faija[3] the one generally used for this purpose is as follows:

Three pats should be made on pieces of glass or other non-porous substance, and their behavior watched under the following conditions:

Pat No. 1 may be left in the air, and No. 2 should be put in water as soon as it is set hard.

Pat No. 3 should be treated in the apparatus for determining

[1] Consult: *Schweizer Bauzeit*, January 12, *1889*.

[2] Description of the "Suchier," "Böhme," and "Brink and Hubner" machines will be found in *Der Portland Cement und seine Anwendungen im Bauwesen*, Berlin, *1892*.

[3] The determination of liability to "checking" or "cracking" (variation in volume) in Portland cements as recommended by *American Society Civil Engineers*, is not as complete as Faija's method, see this JOURNAL, 15, 184.

the soundness of cement. The apparatus consists of a covered vessel in which water is maintained at an even temperature of 110° C; the space above the water is therefore filled with the vapor rising therefrom, and is at a temperature of about 100° C. Immediately the pat is gauged, it should be placed on a rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If, at the end of that period, the pat is still fast to the glass and shows no signs of blowing, the cement may be considered perfectly sound; should, however, any signs of blowing appear, the cement should be laid out in a thin layer for a day or two, and a second pat made and treated in the same manner, as the blowing tendency may only be due to the extreme newness of the cement.

If pat No. 3 shows the cement to be unsound, pats No. 1 and 2 will eventually prove it, but it may be weeks or even months before they develop the characteristics. If pat, No. 2 blows, it may be because it was put in the water before it was set. A cement is considered set hard when it can no longer be marked by the pressure of the thumb nail.

Résumé:

The determination of the value of Portland cement therefore requires the following tests:

First. Chemical analysis.

Second. Determination of fineness.

Third. Determination of tensile strength, including the use of automatic briquette machines as well as an apparatus for mixing the cement with water, as "Faija" mixing machine.

Fourth. Determination of crushing strength.

Fifth. Determination of variation of volume.

RECENT PROGRESS IN THE ANALYSIS OF CATTLE FOODS.[1]

By F. W. Woll.

OUR methods of analysis of cattle foods are essentially the Weende methods, published nearly thirty years ago in *Landw. Versuchs Stationen*, **6**, (*1864*,) 496, by Henneberg. An outline of the methods as given in the place cited, will at once show this to be true.

Henneberg gives the following directions for the determination of the various components of fodders.

1. *Water.*—A few grams of the finely powdered, air-dry sample are heated at 100–110° C., and the results calculated on the original substance.

2. *Mineral Matters* (ash excluding carbon dioxide). 100 to 200 grams are ignited in a muffle oven at as low temperature as possible, and the crude ash weighed, carbon dioxide and char are then determined in a portion of the crude ash, and corrections made accordingly.

3. *Protein.*—Determination of nitrogen and using the factor 6.25.

4. *Crude Fiber.*—A quantity corresponding to three grams water-free substance is taken, and heated for one-half hour in a flat porcelain dish with 200 cc. of a 1¼ per cent. sulphuric acid solution, adding water as it boils away; the solution is then left to settle and the clear liquid pipetted off into a beaker; the sample is again boiled for one-half hour with water, the clear liquid pipetted off into the same beaker as before, and the operations of boiling with 200 cc. of water and pipetting off repeated a second time. 200 cc. of a 1¼ per cent. potassium hydroxide solution are then added and boiled for half an hour, the clear liquid pipetted off into a second beaker, the residue boiled twice with 200 cc. of water, each time uniting the liquid with that already in the second beaker. The residue is then brought on a filter and also that which has settled in the beaker containing the alkaline fluid; the filter is washed until neutral reaction, when the residue in the other beaker is added and the washing repeated and finished by

[1] Read before the World's Congress of Chemists, August 24, 1893.

successive washings with alcohol and ether, drying, weighing, and incineration, which gives the crude fiber by difference.

5. *Ether Extract* (fat).—Complete extraction with boiling anhydrous ether, distillation of the united filtered distillates, and drying the residue at 100–110° C.

Since these methods were first published, our knowledge of the composition of plants and feeding stuffs has been greatly widened; we understand far better than did the writers thirty years ago, what the various groups separated out by the Weende experimenters include, and the conditions which must be observed in each case in order to obtain correct results. But on the purely analytical side we have made but very little progress, the problems have grown more complex every year, and the difficulties of the problems have increased much faster than has our ability to meet them.

In giving a short account of the progress made during recent years in the analysis of cattle foods, I shall take up the various components in the order adopted by Henneberg and still followed by agricultural chemists in general, and shall show the changes which the methods have undergone and suggest the reason for these changes.

As shown by Wilm, Bahring, Baessler, and others, *moisture* cannot be determined in many of our food stuffs by a simple drying in the air, as the fat contained in them will oxidize and the sample thus increase in weight, which means a too low percentage of moisture. Desiccation must, therefore, be conducted in the medium of an indifferent gas; the gas now generally adopted for drying is hydrogen or carbon dioxide, preferably the former. Märcker has further shown that drying above 100° C. may cause formation of resinous substances, and Jenkins found that a volatile oily matter passed off when fodders were heated at 110° in the air or in other gases; the same was observed by Baessler, Wiley, and Cutter. The temperature ought, therefore, never to exceed 100° C. The time necessary for drying will depend on the kind of apparatus used and will vary from four to ten hours; in case of a dry current of hydrogen being passed through the samples, four to six hours will as a rule be found necessary, the velocity of the current being the deciding factor

as to the time required; 90 to 100 bubbles of hydrogen per minute is a maximum velocity (Anderson). The loss of volatile substances will be increased when a very rapid current is passed through the sample. Where the fodders are heated on watch glasses or in open disks in an atmosphere of hydrogen, longer time will be necessary than otherwise, sometimes as much as ten hours, the temperature of drying being all the time that of boiling water.

Ether Extract.—The determination of ether extract has been greatly facilitated by the adoption of the Soxhlet continuous extraction apparatus; the form of extraction tube generally used in the United States is the Johnson extractor, the most recent modification of this being the Caldwell extractor.

The ether extract is determined in the water-free sample, as the air-dry sample extracted with ether will give too high results, for obvious reasons. The ether to be used for extraction must be anhydrous and alcohol-free, as too high results will otherwise be obtained. Numerous comparisons of extraction with ether of different kinds and under varying conditions of drying previous to extraction, have been made by Atwater, Babcock, Wilm, Bahring, Wagner, Märcker and scores of others, and the above points have been fully settled.

As there are several reasons for believing that prolonged drying of any food stuff even at 100° C. modifies the solubility of the fat and the amount of ether extract found, the writer has recently proposed the use of anhydrous copper sulphate in ether extraction. The sulphate will dehydrate both fodder and ether used, and no special precautions for dehydration of either are necessary. The sample of 2-3 grams weighed out may be mixed with about five grams of copper sulphate and the mixture placed in the extraction tube and extracted as usual.

Stellwaag's and Maxwell's investigations have shown the complexity of the bodies making up the ether extract of most feed stuffs. The former found from 0.5 to 34.6 per cent. of insaponifiable components in twenty-five common fodders; lecithin cholesterin, and hydrocarbons have been shown to be present in many cases, as well as coloring matters. It is especially the ether extracts of coarse fodders and roots which contain large pro-

portions of non-glycerides; the extracts of seeds of all kinds are as a rule fairly pure. Various methods have been proposed for the purification of the crude fat, but none have been generally adopted. The purification by means of animal charcoal, proposed by G. Kühn, nearly twenty-five years ago, and proved inaccurate by König in 1871, and by Schulze in 1872, was brought forward again a few years ago by Patterson, who obtained correct results with it. By more recent thorough investigations it has been shown, however, that animal charcoal will retain fat from ethereal solutions passing through it. There is considerable difference in this respect between different kinds of charcoal, making the method entirely unsatisfactory in quantitative analysis.

Crude Protein is determined by multiplying the per cent. of nitrogen found by the Kjeldahl method by 6.25. A great step in advance was made in the adoption of this method (pub. 1883) in agricultural laboratories, and also in the separation of crude protein into albuminoids and amides, according to Stutzer's copper hydrate method (pub. 1880). The Kjeldahl method has been modified by a large number of chemists, and also so as to include nitrate nitrogen; the latter modifications most adopted are those of Jodlbauer and Ulsch.

Crude Fiber.—The Weende method is still the one used by most agricultural chemists. Schulze's method (pub. 1866) and Hönig's (pub. 1891) have both been proved unreliable by several chemists; but on the other hand the investigations made have also proved conclusively that the Weende method gives too low results, contrary to the experience of Kühn and Kern. In comparative determinations the results by the Weende method have come lower in every case, being often only one-half or two-thirds of those found by the Schulze or Hönig method in case of our ordinary cattle foods. It cannot, therefore, be denied that we are still without a satisfactory method for the determination of cellulose or crude fiber in fodders, and use the Weende method only for want of something better.

Ash is determined in a small quantity of the fodder at the present time, not exceeding ten grams. The manner of procedure is otherwise as in the Weende method; or the sample is

carefully burned at a low red heat, the crude ash treated with water, filtered, the residue ignited to whiteness, united with the filtrate, which is then evaporated and the residue heated to low red heat. The reason for this method of proceeding is the easy volatilization of chlorides by direct heating of the ash above red heat, which is necessary to burn the carbon of the ash.

Nitrogen-free Extract is determined by difference, as directed by Henneberg. The errors of analysis incident to the determination of all other components, therefore, enter here and often make the results unsatisfactory. The heterogeneous character of the bodies coming in under this head makes it unfortunate to class all together. A great deal of study has been expended in separating and identifying the various constituents of the nitrogen-free extract of fodders. Pentosans, as galactose, arabinose, xylose were discovered in cattle foods some years ago by Tollens, Schulze and their assistants, and have been found in appreciable quantities in nearly all our common food stuffs. While no satisfactory quantitative method for their determination has yet been devised, the furfurol reaction, worked out by Stone, Allen, and Wheeler, gives a very sharp qualitative test for them.

If determinations of sugar, starch, and possibly also pentosans, could be made in our cattle foods, the rest of the nitrogen-free extract could be classed as *undetermined* and would then include many bodies present in all fodders, the properties of which we yet know very little about, and whose nutritive value is perhaps inferior.

For this short sketch we readily see that more progress has been made in our knowledge of the composition of food stuffs, and in the identification of these constituents than in their estimation. While brought to a certain perfection as far as working details go, the analytical side is yet far behind, and no fully satisfactory system of fodder analysis can be worked out until we are able to classify nutrients more according to their physiological importance than is done in our present methods.

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT, PUBLISHED DURING 1893.[1]

By F. W. Clarke.

To the Members of the American Chemical Society:

YOUR committee, appointed at the last annual meeting respectfully submits the following report, showing the advances made in our knowledge of atomic weights during 1893. The year has been one of reasonable activity in this branch of investigation, and it is thought that all the work actually published within its limits is here summarized and recorded. One partial exception possibly may be made to this statement. Morley's work on oxygen, reported orally at the American Association meeting, and at the Chemical Congress in Chicago, is omitted, for only unofficial abstracts of it have yet appeared in print. That work is of such fundamental importance that it seems best to await its completion, rather than to do it possible injustice by fragmentary notices which might be inexact.

In the "Stas Memorial Lecture," by Professor Mallet,[2] will be found a remarkably full discussion of the theory or philosophy of atomic weight determinations, which should be carefully read by all students in this domain. Taking the life and work of Stas as text and example, Mallet considers the conditions necessary to the fruitful continuation of that work, and throws out many suggestions of great practical value. He particularly advocates the multiplication of interdependent data, in order that errors may be eliminated; and he also recommends the establishment of a special, endowed laboratory, in which a group of trained observers may co-operate towards the attainment of the best results.

The individual atomic weight determinations of 1893 are subjoined.

Boron.—W. Ramsay and Emily Aston[3] redetermine the atomic weight of boron by two distinct processes, one of them being entirely new. First, with many precautions, they estimate

[1] Read at the Baltimore meeting Dec. 28, 1893.

[2] *J. Chem. Soc.*, August, *1893*.

[3] *J. Chem. Soc.*, 63, 207, February, *1893*.

the percentage of water in crystallized borax, $Na_2B_4O_7$, 10 H_2O; all weights being reduced to vacuum standards. The same reduction is also made in their other series, but as they carry out the weights to seven decimal places, the corrections applied go farther than is necessary. In the subjoined tables I give the nearest tenth milligram.

Wt. $Na_2B_4O_7$, $10H_2O$.	Wt. $Na_2B_4O_7$.	Per cent. H_2O.	At. Wt. B.
10.3582	5.4784	47.1099	11.04
5.3440	2.8247	47.1433	10.97
4.9963	2.6379	47.2026	10.85
5.7000	3.0101	47.1912	10.87
5.3143	2.8066	47.1882	10.88
4.9972	2.6392	47.1865	10.885
5.2367	2.7675	47.1524	10.955

Mean atomic weight, B = 10.921, ± 0.010.

In the second series of experiments fused borax was distilled with hydrochloric acid and methyl alcohol, and the residual sodium chloride was weighed. Results as follows:

Wt. $Na_2B_4O_7$.	Wt. NaCl.	At. Wt. B.[1]
4.7684	2.7598	11.015
5.2740	3.0578	10.925
3.2344	1.8727	10.992
4.0862	2.3713	10.879
3.4970	2.0266	10.949

Mean atomic weight, B = 10.952, ± 0.010.

The distillations were conducted in soft glass flasks of about 100 cc. capacity, in which the sodium chloride was dried at about 350°, and finally weighed. It was found, however, that the flasks were somewhat attacked during the process, with liberation of silica, consequently some oxygen in the alkali of the glass had been replaced by chlorine, and the weight of the vessel increased. Another set of distillations was, therefore, made with flasks of hard combustion tubing, and these were slightly attacked also.

Wt. $Na_2B_4O_7$.	Wt. NaCl.	At. Wt. B.
5.3118	3.0761	10.983
4.7806	2.7700	10.955
4.9907	2.8930	10.936
4.7231	2.7360	10.968
3.3138	1.9187	10.992

Mean atomic weight, B = 10.966, ± 0.005.

[1] Atomic weights used in Ramsay and Aston's calculations: O = 16, H = 1.008, Ag = 107.92, Na = 23.05, Cl = 35.45, and Br = 79.95.

As a check upon these results the sodium chloride was dissolved in water, and after filtration precipitated with silver nitrate. The resulting silver chloride was collected on a Gooch filter, dried at 200°, and weighed.

Wt. AgCl.	Per cent. Cl in NaCl.	At. Wt. B. from Cl.
7.5259	60.493	11.071
6.7794	60.515	11.024
7.0801	60.516	11.003
6.6960	60.514	11.039
4.6931	60.479	11.091

Mean atomic weight, B = 11.052, ± 0.010.

From all these results, and after discussing the supposable sources of error in them, the authors conclude that the atomic weight of boron is very nearly eleven.

Still another determination of the atomic weight of boron, by an entirely independent method, is due to Rimbach.[1] Taking advantage of the fact that methyl orange, as an indicator, is unaffected by free boric acid, he titrated solutions of borax with standardized hydrochloric acid, thus measuring the amount of sodium in the salt and thence calculating the value to be ascertained. The borax was prepared in platinum vessels from carefully purified boric acid and sodium carbonate; and the hydrochloric acid used contained 1.84983 per cent. of absolute HCl, determined gravimetrically as silver chloride. In the following table of results the titrated hydrochloric acid is given by weight in grams:

Wt. borax.	Wt. HCl. sol.	Per cent. Na.[2]	At. Wt. B.[2]
10.00214	103.1951	12.07081	10.9646
15.32772	158.1503	12.07138	10.9598
15.08870	155.7271	12.07530	10.9273
10.12930	104.5448	12.07517	10.9298
5.25732	54.2571	12.07435	10.9361
15.04324	155.2307	12.07283	10.9486
15.04761	155.2959	12.07448	10.9356
10.43409	107.6602	12.07176	10.9571
5.04713	52.0897	12.07480	10.9330

Calculating from the sum of all the weights the atomic weight of boron becomes 10.945, ± 0.003.

[1] *Ber. d chem. Ges.*, **26**, 164, February 13, *1893*.

[2] Calculations made with O = 16, H = 1.0032 (Keiser), Na = 23.0575, Cl = 35.4529, and Ag = 107.9376.

Carbon.—Leduc[1] has determined the density of carbon monoxide, deducing thence the atomic weight of carbon. The globe used held 2.9440 of air. Filled with carbon monoxide the latter weighed

2.8470
2.8468
2.8469

Mean, 2.8469

Hence the density of CO is 0.96702, when air = 1, and with

O = 15.88,
C = 11.913,

If O = 16, then C = 12.003,

In a very brief note[2] Wanklyn announces that he has studied a series of hydrocarbons in which the successive steps rise—not by $CH_2 = 14$—but by $\frac{1}{2}(CH_2) = 7$. If these observations are sustained, then the atomic weight of carbon becomes = 6.

Cobalt and Nickel.—Atomic weights determined by Winkler,[3] who starts with weighed quantities of metal, electrolytically deposited. This is then dissolved in a platinum dish in pure hydrochloric acid, and the chlorides produced are finally dried for several hours at 150°. In one set of experiments the chlorine in the chlorides is weighed gravimetrically, as silver chloride; in another set it is titrated with a standard solution of silver. In the first case we have the ratio R:2AgCl, in the other, R:Ag_2. Results as follows, for nickel:

Wt. Ni.	Wt. AgCl. (grav.)	At. Wt. Ni.
0.3011	1.4621	58.9102
0.2242	1.0881	58.9418
0.5166	2.5108	58.8571
0.4879	2.3679	58.9419
0.3827	1.8577	58.9304
0.3603	1.7517	58.8334

Mean result, Ni = 58.9033.

Wt. Ni.	Wt. Ag. (vol.)	At. Wt. Ni.
0.1812	0.6621260	58.9253
0.1662	0.6079206	58.8665
0.2129	0.7775252	58.9584
0.2232	0.8162108	58.8811
0.5082	1.8556645	58.9684
0.1453	0.5315040	58.8631

Mean result, Ni = 58.9104.

[1] *Compt. rend.*, **115**, 1072.

[2] *Phil. Mag.*, (5) **36**, 552, December, *1893*.

[3] *Ztschr. anorg. Chem.*, **4**, 10, *1893*.

The following data were obtained for cobalt:

Wt. Co.	Wt. AgCl. (grav.)	At. Wt. Co.
0.3458	1.6596	59.6044
0.3776	1.8105	59.6609
0.4493	2.1521	59.7215
0.4488	2.1520	59.6577
0.2856	1.3683	59.7081
0.2648	1.2678	59.7480

Mean result, Co = 59.6834.

Wt. Co.	Wt. Ag. (vol.)	At. Wt. Co.
0.177804	0.6418284	59.6495
0.263538	0.9514642	59.6396
0.245124	0.8855780	59.5996
0.190476	0.6866321	59.7311
0.266706	0.9629146	59.6388
0.263538	0.9503558	59.7092

Mean result, Co = 59.6613.[1]

In the case of the cobalt determinations it is of course conceivable that the chloride formed might be contaminated with traces of basic compounds. This question is considered by Winkler in a supplementary communication.[2] The weighed, electrolytic cobalt, deposited upon the surface of a platinum dish, was treated with a solution of neutral silver sulphate. Silver was thrown down, and was washed, dried, ignited, and weighed. Thus a direct ratio was measured between silver and cobalt, involving no intervention of cobalt chloride, and consequently no error due to basic salts. Results as follows:

Wt. Co.	Wt. As.	At. Wt. Co.
0.2549	0.9187	59.7421
0.4069	1.4691	59.6377

The precipitated silver, as a check upon its purity, was dissolved in nitric acid, reprecipitated with hydrochloric acid as chloride, and filtered off. The filtrate, upon evaporation to dryness, gave traces of residue, containing cobalt. The amount of the latter in the first experiment was at most 0.5 milligram, and in the second not over 0.2 milligram. Correcting for these amounts the values found for the atomic weight of cobalt become 59.6356 and 59.6164, respectively. These figures fall within the limits of variation of those found in the first paper,

[1] All calculations with Ag = 107.66 and Cl = 35.37.

[2] *Ztschr. anorg. Chem.*, **4**, 462, *1893*.

and show that the supposed error, if it existed, could not be large. The author admits, however, that the degree of concordance among his experiments is not so great as could be desired. The main purpose of his work was to show the essential constancy of the values, as opposed to the view of Krüss concerning the supposed composite nature of nickel and cobalt.

Molybdenum.—Atomic weight redetermined by Smith and Maas.[1] Sodium molybdate was converted into chloride by heating in a current of pure, dry, gaseous hydrochloric acid. Results as follows with weights reduced to vacuum standards:

Wt. Na_2MoO_4.	Wt. NaCl.	At. Wt. Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078

In mean, Mo = 96.087.

Palladium.—Atomic weight determined by Joly and Leidié[2] by means of potassium palladio-chloride, K_2PdCl_4. In the first series of experiments the salt was dried in vacuo at ordinary temperature. It was then electrolyzed in a solution acidulated with hydrochloric acid, both the palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen, and cooled in an atmosphere of carbon dioxide. Results as follows:

			At. Wt. Pd.	
Wt. salt.	Wt. Pd.	Wt. KCl.	From salt : Pd.	Pd : 2KCl.
1.0255	0.3919	0.5520	105.749	105.643
1.2178	0.3937	0.5551	104.881	105.535
1.2518	0.4048	0.5687	104.923	105.916

This series was rejected by the authors upon finding that the salt retained water. In one experiment 0.23 per cent. of water was found. Accordingly a second set of determinations was

[1] This JOURNAL, **15**, 397, July, *1893*. Results calculated with O = 16, Na = 23.05, and Cl = 35.45.

[2] *Compt. rend.*, **116**, 147, *1893*. Results calculated with O = 15.96, Cl = 35.37, KCl = 74.40, and H = 1.

made in which the palladio-chloride was dried in vacuo at 100°.

Wt. salt.	Wt. Pd.	Wt. KCl.	At. Wt. Pd. Salt : Pd.	Pd : 2KCl.
1.3635	0.4422	0.6186	105.374	106.368
3.0628	0.9944	1.3929	105.545	106.229
1.4845	0.4816	0.6782	105.405	105.694
1.7995	0.5838	0.8206	105.427	105.861

The mean of the values found from the ratio K_2PdCl_4 : Pd is 105.438. If O=16, this becomes Pd=105.702. With O= 15.88 we get 104.910. The KCl values were rejected.

Still another set of determinations was based upon the reduction of the double chloride in a stream of hydrogen, the data being in other respects like the foregoing. Results as follows:

Wt. salt.	Wt. Pd.	Wt. KCl.	At. Wt. Pd. Salt : Pd.	Pd : KCl.
2.4481	0.7949	1.1168	105.560	105.911
1.8250	0.5930	0.8360	105.671	105.656

It is noticeable that these values, in the set K_2PdCl_4 : Pd, run higher than in the electrolytic series. Inasmuch as the latter experiments were made in presence of free hydrochloric acid, it would seem possible that chlorine may have been liberated, preventing complete precipitation of the palladium, and so slightly lowering the apparent atomic weight of the latter. At all events the results obtained are not sharply concordant, and are, therefore, inconclusive.

Barium.—An elaborate memoir upon the atomic weight of barium, by Richards,[1] makes a notable change in the value of that constant. Barium bromide was the compound investigated, and the procedure consisted in titrating its solution with solutions containing known quantities of silver. In many of the experiments the silver bromide thrown down during titration was collected and weighed. From the weights of Ag and of AgBr found, the ratio Ag : Br may be computed as a check on the accuracy of the work.

Full details are given concerning purity of materials, processes, weighings, etc., for which the original memoir must be consulted. The final results are stated in the following columns: First, $BaBr_2$ corresponding to 100 parts Ag. Second,

[1] *Proc. Amer. Acad.*, **28**, 1. Presented Jan. 11, *1893*.

$BaBr_2$ corresponding to 174.080 parts AgBr. Third, percentage of Ag in AgBr.

Exp.	I.	II.	III.
1	137.746	137.783	57.460
2	137.736	137.760	57.455
3	. . .	137.723	. .
4	137.732	. . .	. . .
5	137.735	137.739	57.447
6	137.748	137.748	57.445
7	137.747	. . .	. . .
8	137.740	137.747	57.448
9	137.755	137.748	57.442
10	137.738	137.752	57.451
11	137.747	137.772	57.455
12	. . .	137.726	. . .
14	137.750	137.745	57.443
15	137.756	137.754	57.445
16	137.731	. . .	. . .
17	137.748	. . .	. . .
18	. . .	137.745	. . .
19	137.759	137.758	57.445
Mean, omitting 1 and 2	137.745	137.747	57.448
		Stas found	57.445

The last column, by its agreement with Stas' measurements, serves to confirm the other two, from which the atomic weight of barium is easily computed. From the ratio Ag_2:$BaBr_2$, when Ag = 107.93 and Br = 79.955, Ba = 137.426.

From the ratio 2AgBr:$BaBr_2$, Ba = 137.431.

The value 137.43 then must replace the lower value commonly held hitherto. The new results appear to be thoroughly established and unimpeachable.

Thallium.—Lepierre[1] has redetermined the atomic weight of this metal by several distinct methods. First, by the electrolysis of thallous sulphate in presence of an excess of ammonium oxalate, weighing first the sulphate and then the metal obtained. The latter was dried and weighed in an atmosphere of hydrogen. The corrected weights and results are as follows:

Wt. Tl_2SO_4.	Wt. Tl_2.	At. Wt. Tl.(O = 15.96).
1.8935	1.5327	203.52
2.7243	2.2055	203.67
2.8112	2.2759	203.69

[1] *Bull. Soc. Chim.*, (3) 9, 166, March 20, *1893*.

Secondly, a weighed quantity of crystallized thallic oxide was converted by means of sulphurous acid into thallous sulphate, which was then subjected to electrolysis as in the preceding series. The results are subjoined.

Wt. Tl_2O_3.	Wt. Tl_2.	At. Wt. Tl.
3.2216	2.8829	203.76
2.5417	2.2742	203.53

In the third series of experiments a definite quantity of thallous salt was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which was washed with water and alcohol under various precautions, dried at 100°, and finally weighed in the original crucible.

		At. Wt. Tl.
3.1012 Tl_2SO_4 gave	2.8056 Tl_2O_3	203.57
2.3478 " "	2.1239 "	203.44
2.7591 $TlNO_3$ "	2.3649 "	203.73

Finally, crystallized thallic oxide was reduced in a stream of hydrogen, and the water so formed was collected and weighed.

Wt. Tl_2O_3.	Wt. H_2O.	At. Wt. Tl.
2.7873	0.3301	203.54
3.9871	0.4716	203.82
4.0213	0.4761	203.00

The mean of the eleven figures given for thallium is 203.57, but stated by the author as 203.62. If O=16 this becomes Tl=204.08; and with O=15.88, Tl=202.55. It will be observed that the values found in the individual experiments vary among themselves through a range of over eight-tenths of a unit, and that, therefore, the final mean result is entitled to little consideration. M. Lepierre is evidently unfamiliar with the determinations of his predecessors; for, quite ignoring the admirable work of Crookes, he speaks of the currently accepted value for Tl as resting without proof upon the calculations of Meyer and Seubert. He also neglects to state whether his weighings were reduced to vacuum standards, and he gives no evidence bearing upon the absolute purity and definiteness of the several compounds weighed. The metallic thallium which served as a starting point for the investigations, seems to have been carefully purified.

The Composition of water by Volume.—The volume ratio be-

tween H and O in water, which controls the atomic weight of oxygen as deduced from its density, has been redetermined by Scott.[1] The report published is only in abstract, but the subjoined values for the ratio, H_2:O, are given.

2.0020
2.0024
2.0026
2.0030
2.0022
2.0025
2.0029
2.0023
2.0028
2.0017
2.0022
2.0028

Mean, 2.00245, ± 0.00007.

Combining this mean with the density ratio, O:H::15.882:1,[2] gives for the atomic weight of oxygen the value 15.862.

Scott gives mean results of several other series of experiments, but only this one in detail. The hydrogen was obtained from palladium hydride, and the oxygen from silver oxide. With only an abstract available, the work done cannot be critically compared with Morley's.

The Density of the Principal Gases.—These data, as determined by Lord Rayleigh,[3] having important bearing upon atomic weights, fall properly within the scope of this report. Full details are given as to the apparatus used, and all corrections are applied; such, for instance, as for the difference in volume of the glass globes when filled or exhausted, for the value of gravity at the laboratory in latitude 51°47″, etc., etc. The final results are as follows, with air as unity.

H	0.06960
N	0.97209
O	1.10535

The weights in grams per liter are:

[1] *Proc. Roy. Soc.*, **53**, 130. Read March 23, *1893*.

[2] Rayleigh.

[3] *Proc. Roy. Soc.*, **53**, 134. Received March 4, *1893*.

H	0.09001
N	1.25718
O	1.42952
Air	1.29327

Two of these constants have also been remeasured by Leduc;[1] who gives the following weights for one liter each:

Air	1.29315
N	1.2570

Miscellaneous Notes.—Richards and Rogers, in a paper upon the occlusion of gases by metallic oxides,[2] show that when the oxides of copper, nickel, zinc, and magnesium are compared by the ignition of the nitrates, they retain appreciable quantities of gaseous impurities, such as nitrogen and oxygen, especially the former. The oxides of cadmium, mercury, lead, and bismuth, similarly prepared, contained no gaseous occlusion, excepting a mere trace in the case of cadmium. This observation reveals a possible serious source of error in several determinations of atomic weight, particularly in the cases of zinc and magnesium. In consequence of this fact, the atomic weight of zinc is now under reinvestigation in the Harvard laboratory, the compounds selected for study being the chloride and bromide.

In the study of the rare earths, rough determinations of atomic weight are of great importance in the identification of material. Commonly they are made by the sulphate method, which is familiar to all chemists. Gibbs,[3] however, in a study of these substances, makes use of the oxalates. By ignition, the oxide is left and can be weighed, while the proportion of oxalic acid is easily determinable by titration with permanganate solution. In some cases the oxalates were ignited with weighed quantities of pure sodium tungstate, the increase in weight representing R_2O_3. From the ratio between R_2O_3 and C_2O_3 the molecular weight of the oxide is easily calculated, and agrees well with determinations made by the sulphate process.

Hinrichs, in a series of communications published in the *Comptes Rendus*,[4] attempts to show that Stas' determinations

[1] *Compt. rend.*, 117, 1072.

[2] *Proc. Amer. Acad.*, 28, 200. Presented May 10, *1893*.

[3] *Am. Chem. J.*, 15, 546; November, *1893*.

[4] On the $KClO_3$ work, in 115, 1074. On the lead determinations, in 116, 431.

of atomic weights are vitiated by systematic errors, depending upon the quantities of material weighed. According to him the larger the weight of the substance employed the larger the error; and he constructs curves to represent his views graphically. His mathematical procedure, however, his "method of limits," is not clear, and it savors somewhat of assuming Proutian values in advance, and then regarding variations from them as errors for which corrections should be applied. At all events he fails to point out, on the basis of experimental evidence, how the supposed errors were produced, and he does not show that they could have been of sufficient magnitude to account for the divergencies to be explained. If Stas' work is to be set aside, it can be by experimental researches only.

In a third[1] paper the same author gives his mathematical process in some detail, and still later he discusses Dumas' experiments relative to the atomic weight of oxygen,[2] seeking to show that it is exactly sixteen. Very recently he has also discussed the determinations of the same constant made by Keiser, Cooke and Richards, Morley, and Dittmar and Henderson, reaching the conclusion that the ratio H:O=1:16 rigorously.[3] He objects especially to the use of averages as fallacious, but does not fully establish the legitimacy of his conclusions.

In another journal[4] Hinrichs criticizes Richards' researches upon the atomic weight of copper. After showing that several published determinations of the electrolytic ratio between silver and copper agree quite well with the ratio 108 : 63.5, he takes up in particular Richards' analyses of copper sulphate, and points out that a part of the data correspond with the even values O=16, S=32, and Cu=63.5. The other work of Richards he dismisses as erroneous, but neglects to show wherein the errors lie.

In still another paper[5] Hinrichs proposes to abandon gases like O and H as bases for atomic weight determinations, and to

[1] *Compt. rend.*, **116**, 695.

[2] *Compt. rend.*, **116**, 753.

[3] *Compt. rend.*, **117**, 663.

[4] *Chem. News.*, **68**, 171, October 6, *1893*.

[5] *Compt. rend.*, **117**, 1075.

adopt carbon (diamond)=12 as the fundamental standard, on the ground that it can be exactly weighed. Oxygen and calcium are combined with this as substandards, becoming sixteen and forty respectively.

Replies to Hinrichs' criticism of Stas have been published by Spring[1] and by Van der Plaats.[2] Both writers object to the processes of extrapolation of which Hinrichs makes use, and Van der Plaats shows by tabulation of data that the systematic errors alleged to exist in Stas' experiments are not there. Only fortuitous errors occur, and these are of insignificant magnitude. Furthermore, the ratios determined by Stas are so numerous, so varied, and so concordant in there final results that the presumption in their favor is overwhelming.

In the same paper, indeed, as its main object, Van der Plaats gives the results of a recalculation of Stas' twenty-one ratios by the method of least squares. He does not, however, give his equations nor explain the special form of the method which he used. The results are stated in two tables, one, (A), computed upon the supposition that each ratio is entitled to weight inversely proportional to the square of its mean error; the other, (B), regarding all as of equal weight. O=16 is the base of the system.

	A	B
Ag	107.9244 ± 0.0136.	107.9202.
Cl	35.4565 ± 0.0049.	35.4516.
Br	79.9548 ± 0.0101.	79.9497.
I	126.8494 ± 0.0166.	126.8445.
S	32.0590 ± 0.0085.	32.0576.
K	39.1403 ± 0.0059.	39.1414.
Na	23.0443 ± 0.0043.	23.0453.
Li	7.0235 ± 0.0051.	7.0273.
Pb	206.9308 ± 0.0404.	206.9089.
N	14.0519 ± 0.0078.	14.0421.
NH_4	18.0740 ± 0.0034.	18.0760.
Hence H= . .	1.0055 ± 0.0021.	1.0085.

Another contribution to the Hinrichsian literature is furnished by E. Vogel,[3] who criticizes Stas at considerable length. His

[1] *Chem. Ztg.*, 17, 242, February 22, *1893*.

[2] *Compt. rend.*, 116, 1362.

[3] *Bull. Acad. Bruxelles*, (3), 26, 469.

paper is preceded by adverse reports from W. Spring and L. Henry.

In conclusion I submit a table of atomic weights revised to January 1, 1894. Oxygen=16 is taken as the base of the system, but for provisional reasons only. Before long, with improved determinations, it may be practicable to return to the more philosophical H=1, when the entire system can be transformed once for all into something like permanent shape. A premature transformation of this kind, however, would only work confusion, without corresponding benefit.

Name.	Atomic Weight.	Name.	Atomic Weight.
Aluminum	27.	Neodymium	140.5
Antimony	120.	Nickel	58.7
Arsenic	75.	Nitrogen	14.03
Barium	137.43	Osmium	190.8
Bismuth	208.9	Oxygen	16.
Boron	11.	Palladium	106.6
Bromine	79.95	Phosphorus	31.
Cadmium	112.	Platinum	195.
Caesium	132.9	Potassium	39.11
Calcium	40.	Praseodymium	143.5
Carbon	12.	Rhodium	103.
Cerium	140.2	Rubidium	85.5
Chlorine	35.45	Ruthenium	101.6
Chromium	52.1	Samarium	150.
Cobalt	59.	Scandium	44.
Columbium	94.	Selenium	79.
Copper	63.6	Silicon	28.4
Erbium	166.3	Silver	107.92
Fluorine	19.	Sodium	23.05
Gadolinium	156.1	Strontium	87.6
Gallium	69.	Sulphur	32.06
Germanium	72.3	Tantalum	182.6
Glucinum	9.	Tellurium	125.
Gold	197.3	Terbium	160.
Hydrogen	1.008	Thallium	204.18
Indium	113.7	Thorium	232.6
Iodine	126.85	Thulium	170.7
Iridium	193.1	Tin	119.
Iron	56.	Titanium	48.
Lanthanum	138.2	Tungsten	184.
Lead	206.95	Uranium	239.6
Lithium	7.02	Vanadium	51.4
Magnesium	24.3	Ytterbium	173.
Manganese	55.	Yttrium	89.1
Mercury	200.	Zinc	65.3
Molybdenum	96.	Zirconium	90.6

Discussion.—Dr. Wiley. By our organization we are able to present to American chemists the latest and most accurate numbers for atomic weights. It is a matter for congratulation that this has been accomplished by the American Chemical Society.

UPON THE DETERMINATION OF NITRATES IN POTABLE WATER.

By Augustus H. Gill.

Received February 19, 1894.

PART II.

(b) THE REDUCTION TO AMMONIA.

AFTER a discussion of the various processes for the determination of nitrates by reduction to ammonia, Tiemann concludes with the following:[1] "On account of the unreliability and chances for error which this principle involves, we strongly advise against its use."[2] Tables are given, pp. 208 *et. seq.*, in which the results obtained by reduction with sodium amalgam, aluminum, and the zinc-copper couple, vary from plus ten to minus thirty-eight per cent. which sufficiently illustrate the unreliability.

The objections to any method for such reduction are in brief:

1. The Numerous Corrections to be Applied:
   - I. For free ammonia.
   - II. For nitrates.
   - III. For materials used.
   - IV. For ammonia carried away by the hydrogen.

2. The liability of reducing the organic matter present in the water to ammonia.

3. The time required and chances for error in manipulation.

To the method proposed by Hazen and Clark,[3] they not disdistilling the reduced liquid before nesslerizing are added two more; *viz.*,

4. The colors produced by the Nessler reagent are in many cases not the same *tone* as the standards, and are usually read higher than the amount of ammonia actually found by distilla-

[1] "*Die chem. und bacteriologische Untersuchung des Wassers,*" Tiemann und Gaertner Braunschweig *1890*, 212.

[2] "Entschieden davon abzurathen."

[3] *J. Anal. Appl. Chem.*, 5, 3.

tion;[1] see Nos. 2, 3, and 20 in the following table.

5. When the reduction is finished the liquid in the Nessler tube is not homogeneous, hence the removal of a portion without mixing—which at the same time occasions a troublesome turbidity—does not represent the amount of ammonia actually present.

All these objections might well be waived did the method yield reliable results; but as is shown in the accompanying tables, it is subject to even greater variations than the phenolsulphonic acid process.

RESULTS OF THE ESTIMATION OF NITRATES IN WELL WATERS BY THE ALUMINUM AND PHENOLSULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

No.	P. S. A.	Aluminum direct.	Aluminum crosswise.	Aluminum distilled.	Differences From P. S. A.	Differences Per cent.	Nitrites.	Chlorine.
1	0.4000	0.4323	. .	.	+0.0323	7	none	2.93
2*	1.1500	1.0287 0.8306	. . 0.7407	0.9876 . .	—0.1213 —0.2194	10 23	0.0001	2.78
3*	1.0000	0.8306 0.8235	0.7407 0.6995	. . 0.7407	—0.1694 —0.1765	17 17		2.22
4	0.9000	0.8235	. .	. .	—0.0765	8		2.16
5	0.0090	0.0041	. .	. .	—0.0049	50		0.34
6	0.0085	0.0041	. .	. .	—0.0044	50		0.29
7	0.0500	0.0625	. .	.	+0.0125	40		0.75
8	0.4500	0.3045 0.3538	. . . .	. . . .	—0.1455 —0.0962	33 20		0.96
9	0.0060	0.0288 0.0000	. . . .	. . . .	+0.0228 —0.0060	400 100	none	0.35
10	0.0140	.00329 0.0513	. . . .	. . . .	+0.0189 +0.0373	120 250		0.34
11	0.4200	0.3538	. .	. .	—0.0662	15		0.91
12	0.0000	0.0000 0.0000	. . . .	. . . .	. . . .	. .		0.66
13	0.0400	0.0411	. .	. .	+0.0011	2		0.54
14	0.3250	0.2472	. .	. .	—0.0778	21		1.12
15	0.7000	0.7242	0.6172	. .	+0.0242	3	0.0001	3.40
16	0.7200	0.6748	. .	. .	—0.0452	5	0.0003	2.40
17	0.2500	0.2634	. .	. .	+0.0134	5	0.0002	2.57
18	0.3000	0.3127	0.2469	. .	+0.0127	4	0.0005	2.42
19	1.0000	1.0287	. .	. .	+0.0287	3	0.0000	4.60
20*	1.6000	1.3414 1.4418 1.3579	1.1522 1.2345	. . 1.3168	—0.2500	15	0.0002	2.42

[1] The reason for the difference in tone of the reduced solutions is probably due to the presence of hydroxylamine, as the colors produced can be closely imitated by solutions of this compound. This is unaffected by the excess of alkali, and is with difficulty reduced to ammonia; upon distillation it breaks up into ammonia and nitrogen, thus giving rise to a loss of the latter.

$$3NH_2OH = NH_3 + N_2 + 3H_2O$$

By "crosswise" is meant the comparison of the tubes when looked through diametrically instead of axially as is customary; this was done, as the colors were not the same tone, to see if they could be matched more closely; the "distilled" column indicates the results as obtained by distilling a portion of the reduced liquid in addition to nesslerizing directly, it will be observed that these results are *lower* than those obtained by direct reading.

The method is supposed to be particularly valuable in the presence of relatively large amounts of chlorine; of eleven waters there given having a higher percentage than one part per hundred thousand, *five*, Nos. 1, 15, 17, 18, and 19, are estimated from 3–7 per cent. *higher* and *six*, Nos. 2, 3, 4, 14, 16, and 20, are estimated from 8–20 per cent. *lower* than the results of the phenolsulphonic acid process. Of the remaining waters three are estimated much too high and four as much too low.

Let us consider another table, this time of solutions made to contain definite quantities of nitrate; each letter represents a different and independent observer.

RESULTS OF THE DETERMINATION OF NITRATES IN STANDARD SOLUTIONS BY THE ALUMINUM AND PHENOLSULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

	Aluminum.		Theory.	Phenolsulphonic acid.		
No.	A.	B.		C.	D.	E.
21	0.0800	0.1080	0.0950	0.1020	0.1000	. . .
22	1.2800	1.3000	1.3500	. . .	1.2000	1.3000[1]
23	0.0200	0.0140	0.0160	0.0200	0.0150	0.0180
24	0.8000	0.9500	0.8500	0.8530	0.9500	0.9000
25	2.0500	2.5000	2.2100	2.4500	2.5000	2.5000[2]
26	0.0400	0.0340	0.0380	0.0380	. . .	0.0400
27	0.0800	0.0660	0.0950	0.1000	0.1000	0.0930
28	0.4200	0.3660	0.4250	0.4150	0.4500	0.4000
29	0.4100	0.4040	0.4250	0.4500	0.4250	0.4000
30	0.0300	0.0460	0.0350	0.0370	0.0270	0.0300
31	0.0130	0.0120	0.0140	0.0215	0.0120	0.0150
32	0.0130	0.0180	0.0140	0.0270	0.0150	0.0150
33	0.0580	0.0640	0.0650	0.0620	0.0600	0.0550
34	0.0610	0.0540	0.0650	0.0740	0.0520	0.0550
35	0.0830	0.0880	0.0900	0.0900	0.0920	0.0700

[1] A later determination gave 1.3250.

[2] A later determination gave 2.1300.

No.	Aluminum. Average.	Aluminum. Difference.	Theory.	Phenolsulphonic. Average.	Phenolsulphonic. Difference.
21	0.0940	—0.0010	0.0950	0.1010	+0.0060
22× . . .	1.2900	—0.0600	1.3500	1.2500	—0.1000
23	0.0170	+0.0010	0.0160	0.0176	+0.0016
24× . . .	0.8750	+0.0250	0.8500	0.9010	+0.0510
25× . . .	2.2750	+0.0650	2.2100	2.4833	+0.2733
26	0.0370	—0.0010	0.0380	0.0390	+0.0010
27	0.0730	—0.0220	0.0950	0.0976	+0.0026
28	0.3930	—0.0320	0.4250	0.4216	—0.0034
29	0.4070	—0.0180	0.4250	0.4250	0.0000
30	0.0380	+0.0030	0.0350	0.0313	—0.0037
31	0.0125	—0.0015	0.0140	0.0162	+0.0022
32	0.0155	+0.0015	0.0140	0.0190	+0.0050
33	0.0610	—0.0040	0.0650	0.0590	—0.0060
34	0.0575	—0.0075	0.0650	0.0603	—0.0047
35	0.0855	—0.0045	0.0900	0.0840	—0.0060
		—0.0915			—0.0238
		+0.0055			+0.0184

Numbers 22, 24 and 25, are very obviously incorrectly estimated by both methods; the aluminum process gave in two of these cases results too high; the phenolsulphonic acid process gave likewise in two cases results too high, probably from errors in reading caused by attempting to estimate too deep colors[1] (over 0.1300 parts nitrogen in 100,000).

Considering the other twelve determinations, the aluminum process gave results too low in nine, with a total of 0.0915 parts of nitrogen or *6.6 per cent. too low*, and too high in three with a total of 0.0055 parts of nitrogen or *0.4 per cent. too high*. The phenolsulphonic acid process gave too low results in five cases with a total of 0.0238 parts of nitrogen or *1.6 per cent. too low*, and too high in six cases with a total of 0.0184 parts of nitrogen or *1.3 per cent. too high*.

From this investigation it is evident that the aluminum method, in addition to being more troublesome to execute, yields results even in the presence of chlorine (two parts in 100,000) decidedly lower than the phenolsulphonic acid method; further than this, it was observed that duplicate determinations made by the former process did not present a satisfactory agreement.

[1] This the usual result.

This conclusion I am aware is in direct variance with the statement of Hazen and Clark,[1] who say, "This process (phenolsulphonic acid) with proper precautions, gives results usually too low and often much too low."

In addition to the aluminum process, other methods of reduction have been studied: Fricke[2] states that Förster's—the reduction with metallic iron and caustic potash in presence of alcohol—Schmitt's—the reduction with iron and acetic acid—and Ulsch's,—the reduction by 'ferrum reductum' and sulphuric acid—all yield good results, provided 0.5 gram potassium nitrate be present, these are suitable for the valuation of saltpeters and are obviously not sufficiently refined for the purposes of water analysis. The other method of Ulsch[3] by reduction with iron and sulphuric acid and subsequent measurement of the "deficit of hydrogen" is open to the same objection. One milligram potassium nitrate is equivalent to 1.1 cc. of hydrogen, this corresponds to 1.38 parts nitrogen per 100,000.

Harrow's[4] method, the reduction to nitrate in presence of α naphthylamine and sulphanilic acid is sensitive to 0.04 parts nitrogen per 100,000, or twenty times less delicate than the phenolsulphonic acid process. In my opinion advancement in the estimation of nitric acid for the purposes of water analysis is to be sought, not in any method of reduction to ammonia or nitrous acid, but rather in the formation of organic nitro bodies of high coloring power and constant composition, and with this the writer is already engaged.

In conclusion, I desire to express my indebtedness to Mrs. Richards, Miss Hyams, and Mr. Tuttle, of the Massachusetts Board of Health staff for assistance in making many of the above determinations.

MASS. INST. OF TECHNOLOGY,
LABORATORY OF SANITARY CHEMISTRY,
FEBRUARY, 1894.

[1] *J. Anal. Appl. Chem.*, **5**, 3.

[2] *Ztschr. für. angew. Chemie*, April, *1891*. *Analyst* **16**, 117.

[3] *Ztschr. anal. Chem.*, **20**, 175. *Analyst* **16**, 134.

[4] *J. Chem. Soc., 1891, Trans.*, 320.

DETECTION OF SALICYLIC ACID IN FOOD.[1]

By K. P. McElroy.

SALICYLIC acid has been known for more than half a century, having been discovered in 1838 by Piria[1] in oxidizing the oil of meadow sweet (*Spiraea ulmaria*). But its commercial importance dates back only to 1874 when Kolbe[2] succeeded in making a synthesis of it from sodium phenolate and carbonic acid. In 1860, in conjunction with Lautemann, he devised another synthetic process[3], but as this method involved the use of metallic sodium the product was expensive.

After securing the entire success of his second process, in 1874, Kolbe turned his attention to finding uses for his product. In that and the succeeding year he published a number of papers on[4] its use as a food preservative, as did several of his pupils and assistants, etc.[5] Public attention became attracted to the acid and its use as a preservative spread with great rapidity. In 1877 the French Government[6] found itself obliged to take official action regarding the use in wine and salicylic acid.

Analytical chemists of course were not slow to recognize the new demand on their skill involved by the use of this substance as an addition to food, and methods for its detection were soon elaborated. The number of these methods has yearly increased and at present a fair sized bibliography of analytical literature relative to salicylic acid might be compiled.

The most useful properties of salicylic acid, analytically speaking are that it is volatile with steam, that it is extracted from acid liquids by ether, chloroform, carbon bisulphide or benzol, that it gives a bright purple color with ferric chloride, a green color with copper acetate, and a rose color when boiled with Millon's solution and that when converted into the methyl ester it gives rise to a characteristic odor of wintergreen. The iron test is the one which is universally used for the final recognition of this substance, the previous separation from the food being made either with one of the solvents above named or by distillation. It is extremely delicate, giving a good reaction with a tenth

[1] Read at the Baltimore Meeting, December 27, 1893.

milligram in twenty-five cc. of liquid. The copper test is not particularly delicate, nor is the methyl ester test, at least as far as I am concerned. This latter test has been brought forward particularly by Dr. Curtman, of St. Louis.[7] The test with Millon's solution is given by other substances extractable from foods by ether. The iron test is not given by any substance occurring in food and extracted by ether to my knowledge. Carbolic acid gives the reaction nearest approaching it in color of the common substances, but this substance does not occur in food. Tannic acid, a little of which is sometimes taken up by ether from wines, gives a blackish or greenish color which has a tendency to hide the salicylic color.

In the laboratory of the Department of Agriculture the method which has been most commonly used involves the separation of the salicylic acid by distillation with water vapor. The use of distillation for this purpose, separating salicylic acid from food, I believe was first proposed in an unsigned article[8] appearing in the *Chemiker Zeitung*, in *1882*, presumably from the pen of the editor, G. Krause. It was there stated that the method had been elaborated in the laboratory of that paper. Kolbe used distillation for the analytical separation of salicylic acid in 1880.[9] In using it in this laboratory on the samples of canned vegetables, the analysis of which are recorded in *Bulletin* 13, part 8, of the Division of Chemistry, United States Department of Agriculture, the contents of the can were pulped in a mortar, water added together with a little phosphoric acid, the mixture strained through a bag, and the liquid subjected to distillation. The distillate was then collected in small portions and each portion separately tested with iron chloride. Mr. W. D. Bigelow who was associated with me in the analyses of these goods, and who made the greater portion of the tests, found the best strength of ferric chloride to be about five mgms. to the cc. The salicylic acid has a tendency to accumulate in the later portions of the distillate, and where the amount present is small, there will be hardly any test given by the first fractions. In illustration of this the following experiment may be adduced. Twenty-five milligrams of salicylic acid were dissolved in 250 cc. of water containing a little phosphoric acid and the mixture subjected to distillation, the distillate being collected in twenty-five cc. portions and the sali-

cylic acid estimated colorimetrically. The results may be tabulated as follows:

No.	cc.	Reaction.	Quantity found.
1	25	Distinct but pale	
2	25	Somewhat stronger	
3	25	Still stronger	0.3 mgm.
4	25	" "	0.4 "
5	25	Bright	0.5 "
6	25	"	0.8 "
7	25	"	0.9 "
8	25	"	2.2 mgms.
9	15	"	3.0 "
		Total	8.1 mgms.

I will quote in further illustration of this tendency the method for the determination of salicylic acid in wine described by M. Ince. In this method 210 cc. of wine are mixed with ten cc. of dilute sulphuric acid and the mixture subjected to distillation, the distillate being collected in fifty cc. portions. The first portion is thrown away and the acid estimated in the next two colorimetrically. The quantity found is multiplied by eight, it being assumed that one-eighth of the total salicylic acid will come over in those two fractions when using the amounts of liquid specified.

All the samples of canned vegetables were examined in this way using the fresh contents of the cans. Afterwards, for various reasons, I had the whole series gone over again and the extraction done in a different fashion. The residual contents of the cans had in the meantime been dried and ground to a powder capable of going through a hundred mesh sieve. Portions of this powder were made into a paste, or rather a very stiff dough, with dilute sulphuric acid, and the product placed in an ordinary ether extraction apparatus where it was extracted with ether for several hours. When the ether extract was evaporated to dryness and the residue taken up with water and distilled, the distillate gave the salicylic acid reaction with much greater brilliancy than had the original test, and many samples were found to contain the acid which had before given only doubtful tests or none at all in some cases. The cause of this difference was no doubt the imperfect extraction in the first method of separation, which practically gave only the salicylic acid present in the juice, while

the latter method gave that existing in the solid portions as well. Many reactions were quite faint, so much so as to raise the question of the purpose of the addition of such minute quantities of salicylic acid. The smallness of these quantities was probably due, however, to a cause first pointed out by Kolbe[9] in 1880. Kolbe found that salicylic acid completely disappeared from wine and from water preserved in casks, while in similar samples preserved in glass this disappearance did not take place. Four months, standing, in some cases, were sufficient to cause this disappearance. As an experiment, he placed thoroughly washed cubes of different woods in glass flasks in contact with different solutions of salicylic acid and found that they caused a complete disappearance of the acid after various periods of time, while control samples in which no wood was placed retained their full content of salicylic acid. From the results of this work he drew the inference that woody tissue not only removed the salicylic acid from solution but caused its total destruction in some way, since he could not recover it from the cubes of woods used in the experiments just cited. The woody tissue of the canned vegetables may have caused an action similar to this.

We also use the ordinary "shaking out" method in the Department laboratory to some extent for such goods as beers and wines. The beer or wine is extracted with about half its volume of ether and the extract evaporated to dryness, and the residue taken up with warm water. The resultant solution is tested in the usual way with iron chloride. Between the two processes of separating the salicylic acid, distillation or shaking out with ether, I do not believe there is much choice, though the former is cheaper and more expeditious. The increased purity and sharpness of the reaction given by the distillate as compared with that given by the residue from the ether extract about counterbalance the fact that only a fraction of the salicylic acid appears in the distillate. Objections against the distillation process were raised in 1889 by certain Dutch chemists,[10] on the ground that in the process of fermentation certain "phenol-like bodies" were sometimes formed which interfered with the reaction. "Phenol-like bodies" would interfere not only with the distillation separation but with any other with which I am

acquainted, since phenol is taken up by immiscible solvents from acid solutions precisely as is salicylic acid.

This year three chemists,[11] writing for different German brewing papers, have claimed that in what is called "color" or "caramel" malt a substance exists which gives all the ordinary salicylic acid reactions. The substance is said to exist in many malt extracts rich in isomaltose. J. Brand isolated the substance from color malt and describes all its reactions as being analogous to those of salicylic acid with the single exception of that with Millon's reagent, with which the new substance gave no reaction. I procured a set of color and caramel malts from the World's Fair and tried to obtain a salicylic acid reaction from them, but could not do so. At my request Mr. Bigelow, who not long ago examined a large number of the beers exhibited at the World's Fair, tried a large number of them with Millon's reagent, using it side by side with the iron solution. He reported to me that the Millon's reagent gave salicylic acid in all the samples, irrespective of the reaction upon the ferric chloride. The latter gave salicylic acid in comparatively few. It is only just to say, however, that where ferric chloride indicated the presence of salicylic acid, the reaction given by Millon's reagent was much brighter than where this was not the case.

[1] Piria. Recherches sur la sálicine et les produits qui en dérivent *Ann. de chim. et de phys.*, *1838*, **69**, 281.

[2] Kolbe, H. Vorläufige Mittheilung. *J. prakt. Chem.*, *1873–4*, **8**, 41. Synthese der Paraoxybenzoësäure, ibid, 336. Ueber eine neue Darstellungsmethode und einige bemerkenswerthe Eigenschaften der Salicylsäure, ibid, *1874*, **10**, 89.

[3] Kolbe, H. and E. Lautemann. Ueber die Constitution und Basicität der Salicylsäure. *Liebig's Annalen*, *1860*, **115**, 201.

[4] Kolbe, H. Weitere Mittheilungen über die Wirkungen der Salicylsäure. *J. prakt. Chem.*, *1875*, **11**, 9; Darstellung chemisch reiner Paraoxybenzoësäure durch Umwandlung der Salicylsäure, ibid, 24; Weitere Mittheilung über die Wirkung der Salicylsäure, ibid, 213; Ueber die chemische Natur der Salicylsäure, ibid, *1875*, **12**, 151; Abweisung nicht begründeter Urtheile von Halbchemikern über die antiseptischen Eigenschaften der Salicylsäure, ibid, 161; Die chemische Natur der Salicylsäure, ibid, 151; Chemische Winke für praktische Verwendungen der Salicylsäure, ibid, *1876*, **13**, 106.

Kolbe, H. and E. von Meyer, Versuche über die gährungshemmende

Wirkung der Salicylsäure und anderer aromatischer Säuren. *J. prakt. Chem.*, *1875*, **12**, 133; Ueber die antiseptischen Wirkungen der Salicylsäure und Benzoësäure in Bierwürze und Harn, ibid, 178.

[5] Fontheimer, Karl. Ueber die Wirkung der Salicylsäure als Arzneimittel. *J. prakt. Chem.*, *1875*, **11**, 211.

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Zürn. Die Salicylsäure in der Veterinärpraxis. *J. prakt. Chem.*, *1875*, **11**, 215.

[6] Fauvel, Bergeron, and Bussy (reporter.) Emploi de l'acide salicylique comme agent de conservation des vins. Repport sur une demande d'avis addresse par la chambre de commerce de Paris. Recueil des travaux du comité consultatif d'hygiene *1877*, **7**, 346.

[7] Curtman, C. O. Nachweis der Salicylsäure durch Synthese des Gaultheriaöls. *Pharm. Rundschau*, *1885*, **3**, 155; abs. *Chem. Ztg.*, *1885*, **9**, 1504.

[8] Anonymous (G. Krause?). Nachweis von der Salicylsäure in Nahrungsmitteln. *Chemiker Ztg.*, *1882*, **6**, 619.

[9] Kolbe, H. Zerstörende Wirkung des Holzsubstanz auf Salicylsäure. *J. prakt. Chem.*, *1880*, **21**, 443 and **22**, 112.

[10] Horn, G. A. [Detection of Salicylic Acid in Beer.] *Pharm. Weekblaad* (*1888?*), Nos. 7 and 8; *Apoth. Ztg.*, No. 56; *Ztschr. Nahr. Hyg.*, **2**, 150; *Chem. Centrbl.*, *1888*, 1425.

[11] Erich, E. Ueber die Salicylsäurereaction der Caramelfarbmalze. *Bierbrauer*, *1893*, **24**, 465; abs. *Chem. Ztg. Rep.*, *1893*, **17**, 211.

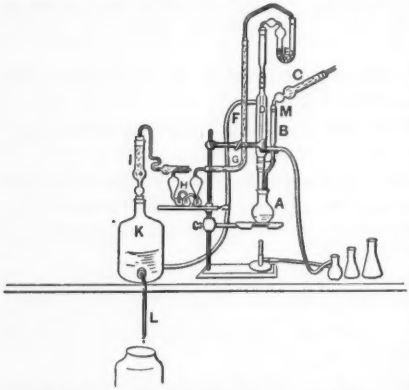
Munsche. Ueber die scheinbare Salicylsäurereaction des isomaltosereichen Malzauszüges, der Caramelmalze und gewohnlichen Farbmalze, etc. *Wochenschr Brauerei*, *1893*, **10**, 739; abs. *Chem. Ztg. Rep.*, *1893*, **17**, 242.

Brand, J. Die scheinbare Salicylsäurereaction bedingenden Korper der Caramelmalze. *Ztschr. ges Brauwesen*, *1893*, **16**, 303; abs. *Chem. Ztg. Rep.*, *1893*, **17**, 242.

A CONVENIENT FORM OF APPARATUS FOR THE ESTIMATION OF CARBONIC ACID.

By Robert H. Forbes.

THE form of apparatus for the estimation of carbonic acid devised by the writer and shown herewith, has been fully tested in our laboratories and found to be accurate, cheap, compact, easily portable, and applicable both to the estimation of carbonic acid in carbonates and to that of carbon in iron by the wet combustion with chromic and sulphuric acids. C is a tube, filled with solid potash, guarding the apparatus from the carbonic acid of the air. The small drop funnel B carries acid to the decomposing flask A. The small condenser D returns most of the water vapor, and the hydrochloric acid to the decomposing flask. The small U tube E, containing a solution of silver sulphate in sulphuric acid, stops hydrogen sulphide and traces of hydrochloric acid. The drying tube F G, of one-half inch combustion tubing, and filled with calcium chloride, finally dries the carbonic acid gas before its absorption at H. The calcium chloride tube I guards the bulbs from moisture, and the aspirating bottle is discharged by the movable tube L.



When used for carbonates, a fifty cc. wide mouthed flask is best, but this must be replaced by a 250 cc. Erlenmeyer flask when making a wet combustion of carbon.

In practice it is found best, after the evolution flask is in position, to turn down the outlet tube L, and regulate the flow en-

tirely from the stop-cock B. Hydrochloric acid rarely gets beyond the condenser, and the downward pitch of the drying tube F G hastens the passage of the carbonic acid gas. The whole apparatus occupies less than two square feet of desk room.

CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, AUGUST 25, 1893.

THE SPECIFIC GRAVITIES OF SOME GEM STONES.[1]

BY A. LIVERSIDGE, M.A., F.R.S., PROFESSOR OF CHEMISTRY, UNIVERSITY OF SYDNEY.

THE following tables contain the specific gravities of some gem stones which were all in the cut and polished condition except in the cases specified. As the specimens were sufficiently free from flaws and mechanical impurities to be cut and polished for jewelry, the specific gravities can be taken as those of typically pure minerals and the results should be more satisfactory than those obtained from ordinary cabinet specimens, unless it can be shown that the specific gravity is altered by the pressure and other treatment they have received during the process of cutting and polishing.

The specific gravities were taken with special care on an Oertling's best chemical balance by direct weighing, *i. e.*, by suspending the specimen in a very small and light metal stirrup in distilled water. A specific gravity bottle was found, as is well known, to give less accurate results.

The temperature at the time of the determination is given in all cases and the results are corrected to 4° C. according to Rossetti's determinations of the density of water.

In the last column are given the extremes of specific gravity as given by F. W. Clarke in his Constants of Nature.

The numbers refer to those in my catalogue of specimens and added in case of future reference.

[1] Read before the World's Congress of Chemists, August 23, *1893*.

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
63	BERYL Beryllium silico-aluminate		20° C.	0.1260	2 6359	2.6312
62	" (five small stones) pale green		"	0.5640	2.7865	2.7816
43	" " " "		21.5° C.	0.1225	2.7282	2.7228
39	" " " "		"	1.0108	2.6826	2.6773
	F. W. Clarke gives a range from 2.650 to 2.725					
	CHRYSOBERYL Beryllium aluminate					
27	Cymophane or cat's eye (three small stones)	Ceylon.	19° C.	0.3615	3.4330	3.4277
14	" " "	"	21° C.	1.8065	3.7147	3.7074
15	" " "	"	"	2.1986	2.9299	2.9241
22	" " "	"	19° C.	0.5193	3.6882	3.6825
24	" " " (four small stones)	"	"	0.6445	3.7040	3.6982
	F. W. Clarke gives a range from 3.597 to 3.860					
45	CHRYSOLITE, Magnesium iron silicate		21.5° C.	0.2186	3.3839	3.3772
	CORUNDUM. Alumina					
33	Adamantine spar	New South Wales.	21.5° C.	1.5550	3.9974	3.9895
	Barklyite (four uncut stones)	" "	18.5° C.	0.5884	3.7382	3.7331
19	Ruby	Ceylon.	21° C.	0.3257	4.0160	4.0081
20	"	"	"	0.2644	4.0060	3.9981
40	" (six small stones)	"	21.5° C.	0.3590	3.9977	3.9898
15	" star	"	19° C.	0.4230	3.8986	3.8925
13	" "	"	21° C.	0.1876	4.0960	4.0880
10	" "	"	20° C.	3.7292	3.9920	3.9850
	F. W. Clarke gives a range from 3.511 to 3.994 for star ruby					
7	Sapphire, pale blue	New South Wales.	19° C.	0.3130	3.8882	3.8822
10	" royal blue	" "	18° C.	0.1398	4.1117	4.1061
17	"	" "	19° C.	0.6486	3.9404	3.9343
38	"	" "	21.5° C.	0.2330	3.9827	3.9751
42	"	" "	"	0.4770	4.0219	4.0140
15	" (four) dark colored	Ceylon.	18.5° C.	0.5050	4.1124	4.1068
5	"	"	20° C.	2.5580	3.9323	3.9254
3	" pale blue	"	19° C.	0.8713	3.9730	3.9668
6	"	"	20° C.	1.3658	3.9784	3.9714

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
7	Sapphire	Ceylon.	20° C.	1.2060	3.9476	3.9407
8	"	"	"	0.8220	4.0039	3.9969
1	" yellow; large "Oriental topaz"	"	"	5.0802	4.0089	4.0019
16	" "	"	19° C.	0.5056	3.9164	3.9103
2	" star	"	"	1.1352	3.9943	3.9881
9	" blue grey star	"	20° C.	4.4812	3.9914	3.9844
11	" star	"	21° C.	2.8314	3.9969	3.9890
12	" "	"	"	0.2973	4.0284	4.0205
29	" "	"	19° C.	1.2374	3.9967	3.9905
	F. W. Clarke gives a range from 3.562 to 4.022					
23	Green sapphire or oriental emerald	New South Wales.				
25	" " (two small stones)	" "	19° C.	0.2872	4.1146	4.1082
23	" "	" "	"	0.9674	4.0041	3.9979
25	" "	Cudgegong, N. S. W.	18.5° C.	0.5996	4 0733	4.0678
2	" " yellow	New South Wales.	20° C.	1.5972	3.9738	3.9668
3	" " pale green	" "	"	2.9772	4.0000	3.9930
	DIAMOND					
61	Diamond, dark uncut octohedron	Bingera, N. S. W.	20° C.	0.2920	3.4762	3.4701
	" five dark colored, uncut		18.5° C.	1.3220	3.5633	3.5585
	" six light " "		"	2.2790	3.5278	3.5230
	F. W. Clarke gives a range from 3.334 to 3.550					
	FELDSPAR. Potassium aluminum silicate					
16	Moonstone	Ceylon.	21° C.	0.7370	2.5877	2.5826
17	"	"	"	0.3534	2.5833	2.5782
18	"	"	"	0.2288	2.5823	2.5772
	F. W. Clarke gives a range from 2.5702 to 2.5950					
	GARNETS					
44	Garnet, almandine. Iron aluminum silicate		21.5° C.	0.1510	4.0266	4.0187
49a	" two specimens "		"	0.1248	4.0519	4.0439
59	" three " "		20° C.	1.3708	4.0058	3.9088
37	" two " "		21.5° C.	0.3038	4.1389	4.1308
41	" two " very dark		"	0.2558	4.0862	4.0792

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
60	Garnet		20° C.	1.3768	4.0637	4.0566
64	" three specimens		"	0.3280	4.1000	4.0928
65	" two " very dark		"	0.2748	3.9458	3.9389
37a	" two " "		21.5° C.	0.5714	4.2515	4.2431
53	" cinnamon stone. Calcium aluminum silicate		20° C.	0.4566	3.6448	3.6384
28	" " "		19° C.	0.4939	3.6420	3.6363
54	" " " less full of air bubbles		20° C.	0.5157	3.7342	3.7276
	F. W. Clarke gives a range for almandine of from 3.900 to 4 236.					
	" " " " cinnamon stone " 3.252 to 3.609.					
50	LAPIS LAZULI, four peices cut and polished for stud links		21.5° C.	1.3560	2.7684	2.7629
	PEARLS. Calcium carbonate					
46	Pearl, three specimens	Ceylon.	21.5° C.	0.2841	2.7291	2.7237
47	" " " very irregular	Torres Straits.	"	1.1422	2.6837	2.6784
48	" " "	" "	"	0.4510	2.6845	2.6792
	QUARTZ. Silica					
56	Rock crystal		20° C.	0.2255	2.6877	2.6830
	F. W. Clarke gives a range from 2.61 to 2.6507 at 0° C					
57	Amethyst		20° C.	0.4756	2.6481	2.6434
	" purchased at	Oberstein.	18° C.	5.2408	2.6565	2.6529
	F. W. Clarke gives a range from 2.659 to 2.744					
26	Rose Quartz, two specimens	Ceylon.	19° C.	1.1598	2.6674	2.6632
	F. W. Clarke gives a range from 2.651 to 2.658					
	Cairngorm, purchased at	Oberstein.	18° C.	22.4670	2.6555	2.6519
	" "	"	"	15.6290	2.6553	2.6517
	" "	"	"	13.3554	2.6567	2.6531
	" brown "	"	"	3.9084	2.6567	2.6531
	F. W. Clarke gives a range from 2.651 to 2.658 (smoky)					
8	Fibrous Quartz, "Cat's eye,"	N. S. W., West. Dist.	18.5° C.	0.2636	2.6703	2.6667
34	Opal. Hydrous silica, two specimens	New South Wales.	19° C.	0.1150	2.0105	2.0074
35	" " " " "	"	21.5° C.	0.1858	2.0690	2.0649
6	" " " flawed	"	19° C.	0.3616	2.0769	2.0746

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
	SPINELS. Magnesium aluminate					
8	Spinel, dark blue	Ceylon.	18° C.	0.3306	3.6392	3.6343
35	" puce	"	21.5° C.	0.3468	3.5900	3.5829
36	" dark puce	"	"	0.1616	3.5831	3.5761
	F. W. Clarke gives a range from 3.48 to 3.77					
	TOPAZ. Aluminum silico-fluoride					
1	Topaz, colorless	New South Wales.	19° C.	1.5213	3.5602	3.5547
18	" "	" "	18° C.	11.6010	3.5509	3.5461
58	" "	" "	20° C.	0.6334	3.5110	3.5048
32	" two white	Ceylon.	21.5° C.	2.0280	3.5717	3.5647
51	" "	"	20° C.	0.4282	3.5330	3.5268
31	" yellow Brazilian	Brazil.	21.5° C.	0 3162	3.5728	3.5658
30	" pink " burnt	"	19° C.	1.0845	3.5406	3.5372
52	" " "	"	20° C.	0.8920	3.6257	3.5195
13	" "	"	19° C.	0.4413	3.4676	3.4622
55	"	"	20° C.	0.6585	3.5691	3.5628
	F. W. Clarke gives a range from 3.439 to 3.597					
12	TOURMALINE Aluminum boro-silicate					
	" brown colored specimen	Ceylon.	19° C.	0.4835	3.0087	3.0040
	F. W. Clarke gives a range from 2.997 to 3.243 and from 3.035 to 3.068 for brown tourmalines					
5	TURQUOISE. Hydrous aluminum phosphate	Sinai.	19° C.	0.3440	2.7388	2.7345
	F. W. Clarke gives a range from 2.426 to 2.651					
	ZIRCONS. Zirconium silicate					
4	Zircon, red	New South Wales.	19° C.	0.4026	4.4783	4.4714
9	"	" "	18° C.	0.3118	4.7822	4.7757
10	" cut and polished	" "	18.5° C.	1.8145	4.7191	4.7127
14	" pale green	Ceylon.	19° C.	0.4160	4.5021	4.4951
	F. W. Clarke gives a range from 4.047 to 4.709 at 21° C					

NOTES ON THE GRANDEAU METHOD FOR THE DETERMINATION OF HUMUS IN SOILS.

By Harry Snyder.

Received January 18, 1894.

THE Grandeau method for the determination of humus in soils, without some modifications, is open to serious objections: (1) It is difficult to obtain a complete extraction of the humus materials with ammonia, as ordinarily carried on, especially when the soil is very fine and of a clayey nature. (2) The filtration is frequently so slow that a week is sometimes required before the filtrate becomes clear. (3) During all of this time the laboratory is so filled with the fumes of ammonia as to seriously interfere with other lines of work.

To say the least, the present method is slow, cumbersome, and gives unsatisfactory results with many kinds of soils. The author has had in use during the past year, a few simple modifications, that have given good results.

After treatment with the dilute acid, the soil is transferred to either a glass-stoppered bottle, or a glass-stoppered Erlenmeyer flask of 100 cc. capacity, using fifty or sixty cc. of the dilute ammonia solution for that purpose. The contents of the bottle or flask are then well shaken at frequent intervals, and then allowed to settle. After settling, the dark colored solution is decanted into a filter, a fresh fifty cc. portion of the dilute ammonia solution is then added to the flask, and the same treatment repeated. It usually requires three or four such treatments before the filtrate becomes clear; the contents of the flask are then brought on to the filter, and require but little farther washing in the usual way before this part of the operation is completed. While the second, third, and fourth treatment with the ammonia is being carried on, the first portion of the filtrate can be evaporated on the water bath, and thus save time when that part of the operation is reached. The most progress can be made by making as large a number of determinations at one time as a person can conveniently take care of, so as not to unnecessarily hurry the operations, nor lose too much time in

making the humus determinations of the soil. A separate room for such work is a great convenience.

The results obtained by this method of treatment are much higher than those obtained when working in the usual way. This is to be expected, inasmuch as more complete extraction of the humus materials are obtained by using the glass-stoppered flasks. Duplicate results with the ordinary Grandeau method are far from being concordant, while with the glass-stoppered flasks reasonably concordant results are secured.

The Grandeau method for the determination of humus, when properly carried out, is capable of giving results that are of practical agricultural value. The examination of a few typical cases out of over a hundred samples of soil examined in the laboratory of the Minnesota Experiment Station, during the past two years, will show that the results obtained by the modified Grandeau method are well worth all of the time and labor that has been spent. Before examining the results, two points are to be noted:

First. There are many other organic compounds of equal agricultural value that are not included in the ammonia extract. Take for example any of the soils that show from ten to fifteen per cent. of volatile matter. The combined water, carbon dioxide, and humus, as well as volatile mineral matters account for sixty to seventy-five per cent., only, of the volatile material, leaving twenty-five per cent. of the volatile organic materials not accounted for. These organic materials, may, in time, become soluble in the ammonia solution, and finally be classed as humus materials. The Grandeau method gives us no idea of the extent to which these organic substances may be present in the soil.

Second. Along with the humus soluble materials are variable amounts of phosphoric acid. A careful study of the total phosphates, humus and phosphates soluble with the humus fails to indicate any chemical combination between the humus and the ammonia soluble phosphates. At this point another serious difficulty presents itself: Some soils which are rich in both phosphoric acid and lime, will give up some of their phosphoric acid to the dilute hydrochloric acid solution

that is first used to remove the lime. This appears to be quite prominent with some of the native soils that are particularly rich in total phosphates, humus, and lime. The analyses of many of these soils showed that the phosphates soluble in the dilute ammonia, and supposed to be in combination with the humus as available phosphoric acid, was less, in many soils, even when the humus was found to be high, than in other soils that were known to be far less fertile. A repetition of the work showed that the dilute hydrochloric acid used in removing the high percentages of lime, also removed a large portion of the phosphates that would have been soluble in the ammonia. Is not this phosphoric acid equally as valuable, agriculturally, as that soluble in the dilute ammonia? Qualitative tests can easily be made of the hydrochloric acid washings, to determine the presence or absence of phosphates.

In the native soils there is quite a close relation between the humus, as determined by the modified method, and the total nitrogen. The table given, shows the amounts of humus and nitrogen, as well as the ratio between the two, in a number of native soils, and soils that have been cultivated for various periods without the use of fertilizers. The volatile matter given includes both the total organic matter and the combined water, the carbon dioxide, hygroscopic moisture, etc., having been separately determined and subtracted from the total volatile matter.

RATIO OF NITROGEN TO HUMUS.

Description of soil.	No. of soil.	Total volatile per cent.	Humus per cent.	Total nitrogen per cent.	Ratio.
Virgin soil	203	15.55	5.34	0.38	13.97
10 years cultivation	298	5.58	3.02	0.25	12.10
Virgin soil	202	8.10	5.16	0.41	12.60
10 years cultivation	236	5.48	2.87	0.21	13.60
Virgin soil	272	14.29	5.16	0.39	13.23
8 years cultivation	309	9.67	3.16	0.25	12.60
6 " "	224	10.90	5.12	0.38	13.20
Native prairie	224	12.05	4.04	0.37	10.91
10 years cultivation	312	8.15	2.60	0.22	11.80
6 " "	249	11.50	4.92	0.41	12.00
10 " "	208	7.13	2.68	0.24	11.18
8 " "	210	4.04	3.02	0.24	12.60

Description of soil	No. of soil.	Total volatile per cent.	Humus per cent.	Total nitrogen per cent.	Ratio.
10 years cultivation	257	8.68	2.48	0.19	13.10
15 " "	234	6.47	2.48	0.20	12.40
3 " "	220	12.40	4.17	0.37	11.28
3 " "	218	6.56	3.73	0.30	12.43
20 " "	261	8.73	2.84	0.26	11.31
30 " "	279	8.31	1.80	0.16	11.25
40 " "	242	7.04	2.41	0.21	11.50
6 " "	222	10.33	3.42	0.28	13.00
18 " "	269	9.44	3.91	0.34	11.50
25 " "	290	3.54	2.27	0.17	13.35
6 " "	273	8.13	4.18	0.37	11.33
18 " "	249	7.94	2.04	0.17	12.00

There is, on the average, about twelve parts of humus in the soil, as determined by the method given, to every one part of nitrogen. In the long cultivated soils which have received no fertilizers, the nitrogen and the humus have decreased in about the same ratio. The losses and relationships are not in strict accordance to a mathematical ratio, but it is sufficient to show that there is a relationship between the humus and the nitrogen in a virgin soil, and in soils which have been cultivated without the use of fertilizers.

UNIVERSITY OF MINNESOTA,
LABORATORY OF THE
COLLEGE OF AGRICULTURE.

NOTES.

The Opening of the Kent Chemical Laboratory of the University of Chicago.—In response to invitations sent out by the authorities of the University of Chicago to the chemists throughout the country to be present at the formal opening exercises of the Kent Chemical Laboratory, January 1 and 2, 1894, about fifty chemists assembled in the auditorium of the laboratory, at two o'clock P. M., January 1. It was proposed that the first meeting should be a conference of teachers of chemistry. President Harper delivered a brief address of welcome and closed by saying that Prof. Remsen had consented to act as chairman of the conference—Prof. Remsen then took the chair and after a few introductory remarks introduced Prof. Paul. C. Freer, of the

University of Michigan, who had been invited to open the discussion by reading a paper on, "The Teaching of Chemistry in Secondary Schools and Colleges." After Prof. Freer's paper which was very suggestive, a general and spirited discussion ensued which was alike enjoyable and helpful to all present.

At six o'clock dinner was served at the hotel Windermere to the visiting chemists who were the guests of the University. The dinner was elegant in every particular. No "after dinner speeches" were made but during the progress of the courses president Harper announced that it had been proposed that the chemists present, organize a chemical society of some sort and as he knew very little about it he would call on Prof. Nef to state the nature of the proposed plan — Prof. Nef said that the idea was to organize a society of teachers of chemistry to meet at least once a year to discuss methods of teaching chemistry. He invited discussion and after remarks by a few chemists, a motion was made and carried, referring the whole subject to a committee, to be appointed by the chairman, to report to a meeting to be held the next morning at nine o'clock, in the auditorium of the Kent Laboratory. President Harper asked Prof. Remsen to appoint the committee, and he named: Profs. A. B. Prescott, J. U. Nef, P. S. Baker, W. W. Daniells, and A. V. Young.

Immediately after the dinner the chemists returned to the auditorium of the laboratory where at eight o'clock the dedicatory exercises began. President Harper with Mr. Sidney A. Kent headed the procession, followed by Prof. Remsen, Rev. Dr. Northrup, Prof. Nef, the visiting chemists and the faculty of the University. The visiting chemists occupied front seats in the audience while the speakers, Mr. Kent, and the faculty sat on the platform. The dedicatory prayer was delivered by Dr. Northrup, of the University of Chicago. President Harper then delivered a short address in which he read the letter of donation from Mr. Kent. It was as follows:

"Mr. William R. Harper, president of the University of Chicago — My Dear Sir: I hereby give this building, fully furnished and completely equipped, to the University of Chicago as a chemical laboratory for the use of this and future generations. Trusting that the standard of educa-

tion will be such as to command the respect not only of this country but of the civilized world. Very Truly Yours,

"Chicago, Jan. 1, 1894." S. A. KENT.

Prof. Ira Remsen, of Johns Hopkins University, who had planned the laboratory was then introduced. He made a very graceful address and at the close he thanked Mr. Kent in behalf of the chemists of the country for the substantial aid he had given the science in building so magnificent and complete a workshop.

Prof. J. U. Nef, under whose immediate supervision the laboratory had been built, and who planned most of the detail of the interior fittings was then introduced. He delivered an interesting address entitled, "Important Factors in the Development of a Research Laboratory."

At the conclusion of Prof. Nef's address, president Harper called on Prof. A. B. Prescott, of the University of Michigan, as the oldest teacher of chemistry present to make some remarks. Prof. Prescott delivered a brief impromptu address in his usual happy and pointed style. At the conclusion of the addresses a reception was held in the Halls of the laboratory.

The laboratory and equipment has cost Mr. Kent $235,000.00, and it is very handsome, convenient and complete. It is to be hoped that the plan with detailed description will be published before long.

Mr. Kent is the brother of the founder of the Kent Chemical Laboratory, of Yale University. In the vestibule of the main entrance on the east wall is a handsome medallion bas-relief of Mr. Kent and below it is the dedicatory inscription which reads thus:

"This building is dedicated to a fundamental science in the hope that it will be a foundation stone laid broad and deep for the temple of knowledge in which as we live, we have life.—Sidney A. Kent."

On the morning of January 2, at nine o'clock, the visiting chemists assembled to hear the report of the committee appointed the night before at the dinner. The report provided for a conference of chemists to be held annually at such time and place as may be decided each year by the conference. No organization was made other than the formation of a standing

committee of three (3) members who are to make the necessary arrangements for the meeting, the chairman of the committee is to act as secretary of the conference. The committee for 1894 consists of Profs. J. U. Nef, P. S. Baker, and P. C. Freer. The object of the conference is to discuss methods of teaching and no papers on research are to be read. The meetings are to be arranged so as not to conflict with the meetings of the American Chemical Society and it was the sense of the meeting that whenever possible the conference should be held in conjunction with the meeting of the American Chemical Society.

The Winter Convocation of the University was held in Central Music Hall, January 2, at eight o'clock P. M. The convocation address being delivered by Prof. Ira Remsen who took as his subject, "The Chemical Laboratory." He spoke of the origin and development of the modern chemical laboratory and of the character of the work which had been done in the great laboratories of the world; of the work which had been accomplished in this country and of the prospects for the future. His address was highly entertaining and was enjoyed by a large audience composed of the faculties, official guests, students, and friends of the University. After the exercises a reception was held by the president in honor of Prof. Remsen in the foyer of the Music Hall.

The committee of arrangements who had charge of all of the exercises consisted of Profs. J. U. Nef, R. D. Salisbury, C. A. Strong, W. S. Stratton, and J. Loeb.

They are to be congratulated on the success of their management.

W. L. DUDLEY.